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VALIDATION OF THE EKMA MODEL USING HISTORICAL AIR QUALITY DATA

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Historical air quality and emissions trend data for the Los Angeles region were used to check the EKMA isopleth method of relating ozone concentration changes to precursor emission changes. Trends in ozone and ozone precursors (NMHC and NO_x) were estimated from data for the period 1964 to 1978.

Emission trend calculations show that basinwide hydrocarbon emissions decreased continually, with a net reduction of 29% over the study period. Estimated basinwide NO_x emissions rose rapidly from the middle 1960s to the early 1970s and then levelled off; the net increase over the study period was 34%.

Sensitivity analysis reveal that predicted ozone trends are moderately sensitive to the specific EKMA simulation conditions. Predicted ozone trends are extremely sensitive to the NMHC/NO_x ratio.

The EKMA model performs fairly well in the validation studies. There is, however, a general tendency for predicted ozone trends to underestimate historical decreases in actual ozone trends. One reason for the discrepancy appears to be error in the choice of an NMHC/NO_x ratio.

Further research should be conducted to test the EKMA chemical-kinetic mechanism and to check the equivalency between ambient and EKMA NMHC/NO_x ratios.

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ABSTRACT

Historical trend data for the Los Angeles region are used to check the EKMA isopleth method of relating ozone concentrations to precursor control. Trends in the ozone precursors (NMHC and NO_x) are estimated from emissions and ambient data for the period 1964 to 1978; these precursor trends are entered into the EKMA method to predict historical ozone trends; the predicted ozone trends are then compared to actual ozone trends as a test of the EKMA method.

Emission trend calculations show that basinwide hydrocarbon emissions decreased continually, with a net reduction of 29% over the study period. Estimated basinwide NO_x emissions rose rapidly from the middle 1960s to the early 1970s and then levelled off; the net increase over the study period was 34%. Ambient precursor trends measured at several monitoring sites agree quite well with the emission trend estimates.

Sensitivity analyses reveal that predicted ozone trends are moderately sensitive to the specific EKMA simulation conditions. Predicted ozone trends are extremely sensitive to the NMHC/NO_x ratio.

The EKMA model performs fairly well in the validation studies. There is, however, a general tendency for predicted ozone trends to underestimate historical decreases in actual ozone trends. This discrepancy apparently cannot be accounted for by error in estimated precursor trends, meteorological fluctuations in actual ozone trends, or sensitivity to varied EKMA simulation conditions. The reason for the discrepancy appears to be error in the choice of an NMHC/NO_x ratio.

The study indicates that it may be important, in some applications, to use the most realistic, area-specific EKMA simulation conditions (such as inclusion of post 8 AM emissions). It is even more critical to obtain an accurate estimate of the NMHC/NO_x ratio. Further research should be conducted to test the EKMA chemical-kinetic mechanism and to check the equivalency between ambient and EKMA NMHC/NO_x ratios.

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CHAPTER 1

INTRODUCTION AND SUMMARY

The Empirical Kinetic Modeling Approach (EKMA) has recently been proposed as a method for evaluating ozone control strategies (Dimitriades 1977a; EPA 1977, 1978a, 1980). Before the EKMA method is accepted as a reliable technique for control strategy analysis, it should be subjected to validation studies. The purpose of this report is to test the EKMA method using historical trend data for the Los Angeles area. Specifically, trends in the ozone precursors (NMHC and NO_x) are estimated from emissions and ambient data for the period 1964 to 1978; these precursor trends are entered into the EKMA method to predict historical ozone trends; the predicted ozone trends are then compared to actual ozone trends as a test of the EKMA method.

In this study, we find that analysis of historical trend data from Los Angeles is an appropriate and useful way of validating the EKMA method. Historical trend analysis also provides a very convenient format for illustrating the sensitivity of the EKMA method to various inputs, such as the NMHC/NO_x ratio and the choice of specific photochemical simulation conditions. The historical trend data, however, are not only of interest with respect to testing EKMA but also of interest in-and-of themselves. By conducting a detailed analysis of precursor emission trends, we can show how emissions for individual source categories have changed due to controls and source growth, and how total emissions have changed as a net response to trends for individual source categories. By examining trends in ambient precursor data, we can check the emission trend estimates and verify that control programs and source growth have had the anticipated effects. By analyzing historical ozone trends, we can investigate whether or not the ozone trends make sense in light of precursor changes and meteorological fluctuations. Thus, this study is useful not only as a means to validate EKMA, but also as a means to understand the air quality effects actually being produced by on-going control programs in Los Angeles.

THE EKMA METHOD

The EKMA method for evaluating ozone control strategies is based on an isopleth diagram relating ozone levels to initial concentrations of NMHC and NO_x (see for example, Figure 26 on page 70).* The ozone isopleth diagram is generated by a chemical-kinetic model calibrated to smog chamber data. The chemical kinetic model has the capability to consider various irradiation times, dilution rates, solar insolation profiles, emission profiles, hydrocarbon composition mixes, and levels of transported ozone.

The EKMA diagram is not intended by EPA to be used in an absolute sense, i.e. to predict specific afternoon ozone levels for specific morning precursor concentrations. Rather, the EKMA isopleths are intended for use in a relative sense for control strategy evaluation, i.e. to predict changes in ozone levels for given percent changes in precursor levels. The procedure for control strategy analysis with EKMA is essentially to locate base year coordinates on the isopleth diagram by specifying the base year ozone level and NMHC/NO_x ratio, and to predict ozone for future years by factoring the NMHC and NO_x coordinates of the base year according to future emission changes.

Because the EKMA method is intended for use in a relative sense to estimate the sensitivity of yearly ozone levels to changes in yearly precursor levels, the most appropriate validation tests for the method should involve historical trend data. Specifically, the EKMA isopleth method can be tested by using it to predict historical ozone trends based on historical precursor changes, and by comparing these predictions to actually observed ozone trends. Trijonis and Hunsaker (1978) conducted validation studies of the EKMA method using historical data for several sites in the Los Angeles region during the period 1964 to 1975. In some cases, significant discrepancies were found between the isopleth predictions and actual ozone trends.

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*A note on terminology: Because of historical precedence, we have decided to use the term "NMHC (nonmethane hydrocarbons)" rather than the more exact term "NMOC (nonmethane organic compounds)". Also, we have decided to use the term "ozone" throughout this report despite the fact that all the ambient data considered herein (except at the San Bernardino study site) actually represents "oxidant" data taken with the KI monitoring method.

In the present study, we will expand and improve upon the previous study of Trijonis and Hunsaker by updating the data base to cover the period 1964 to 1978, by refining some of the inputs to the study (emission trend estimates, ambient precursor trend estimates, data for the ambient NMHC/NO_x ratio, and EKMA simulation conditions), and by conducting a more thorough analysis regarding the causes of any observed discrepancies.

THE LOS ANGELES STUDY REGION

The Los Angeles region offers a uniquely excellent opportunity for EKMA validation studies based on historical trend data. Only Los Angeles can provide nearly two decades of high-quality, spatially-resolved, long-term trend data for ambient concentrations of ozone, hydrocarbons, and NO_x. Only Los Angeles can provide independent data sets regarding the NMHC/NO_x ratio from several monitoring programs. Los Angeles is also unique in regard to the excellence of data for emission trend analysis; the Los Angeles area has unusually good information regarding existing emission levels, source growth rates, and source control levels. Furthermore, substantial changes in historical precursor levels are required for an adequate test of the EKMA method, and we know that Los Angeles has undergone significant decreases in hydrocarbons and increases in NO_x since the middle 1960s (Trijonis et al. 1978; Trijonis 1980). Los Angeles, of course, is also an intriguing study area because it has a very severe photochemical smog problem and because there is a current controversy regarding the recent lack of air quality improvement.

The EKMA validation studies conducted herein cover the time period 1964 to 1978. In order to provide robust data sets for the analysis, three-year averages (1964-1966, 1967-1969, 1970-1972, 1973-1975, and 1976-1978) of air quality data are used. The period 1964-1966 serves as a base period for the study. Tests of the EKMA model are made by comparing predicted ozone trends to actual ozone trends at each subsequent three-year interval.

This study uses four basic data sets: information on the 6-9 AM ambient NMHC/NO_x ratio, estimates of historical emission trends, ambient precursor trend data, and ozone trend data. The base period (1964-1966) 6-9 AM

NMHC/NO_x ratio is determined by examining ambient data from several monitoring programs of the early 1970s and by extrapolating the results back to 1964-1966 based on historical precursor trends. Historical trends in NMHC and NO_x emissions are documented through a new and comprehensive analysis of all major source categories (see Appendix A). Ambient precursor trends are examined at 9 sites for NMHC and 10 sites for NO_x. Ambient ozone trend data from 13 sites are considered. It should be noted that the ambient data for NMHC, NO_x, and ozone have been subjected to several correction and adjustment procedures (discussed herein) to make these data consistent for the purpose of trend analyses.

In this report, the basinwide EKMA isopleth model (based on the maximum ozone during a 10-hour irradiation) is tested against historical trends for the yearly basinwide 1-hour ozone maximum. To provide greater generality in validating the isopleth approach and to increase the number of test cases, four individual sites are also chosen for analysis: Azusa, Downtown Los Angeles (DOLA), Anaheim, and San Bernardino. The validation studies at these four sites are conducted using EKMA isopleths that are specific to the time of occurrence of maximal ozone at those locations. Two ozone air quality indices, yearly 1-hour maximum concentration and 95th percentile of daily maximum concentrations, are used at each of the four individual study sites.

SUMMARY

The purposes of this study are to characterize historical precursor trends in the Los Angeles region using both emissions data and ambient data (Chapter 2); to document historical ozone trends (Chapter 3); to investigate the sensitivity of EKMA predictions to the NMHC/NO_x ratio and to the choice of specific simulation conditions (Chapter 4); and to test the EKMA isopleth model by comparing predictions of historical ozone trends with actual ozone trends (Chapter 5). The following subsections summarize our findings and conclusions. For convenient referral, the summary is organized according to the order of the chapters.

Historical Precursor Trends (Chapter 2)

- Estimated basinwide emissions of reactive hydrocarbons (RHC) decreased continually during the study period, with a net reduction of 29% from 1965 to 1977. The predominant part of this reduction was due to decreases in emissions from light-duty vehicles (the largest source category); light-duty vehicle RHC emissions decreased 40% from 1965 to 1977 despite a 54% increase in traffic levels. Organic solvent emissions also underwent a significant (30%) decrease, with this reduction basically occurring between 1965 and 1974.

- Estimated basinwide NO_x emissions rose rapidly from 1965 to 1973 and then basically leveled off. The net increase over the entire study period, 1965 to 1977, was 34%. The predominant part of this rise was due to a 55% increase in NO_x emissions from light-duty vehicles (the largest source category). The net increase in light-duty vehicle NO_x from 1965 to 1977 basically represented traffic growth. Light-duty vehicle NO_x emission factors for new cars jumped upward in the late 1960s, but by 1977 the fleet-averaged NO_x emission factor was reduced back to the 1965 level due to the new car NO_x emission standards of the 1970s. NO_x emissions from heavy-duty vehicles and residential/commercial/industrial fuel burning also increased significantly from 1965 to 1977, reflecting growth in traffic and natural gas usage, respectively. Power plant NO_x emissions decreased slightly from 1965 to 1977.

- Emission trends differ somewhat among the various individual source areas affecting the ozone study sites, reflecting differences in growth rates and source types within those areas. Comparing estimated emission trends with ambient precursor trends for each source area, we find very good agreement, especially when the data are viewed in an overall sense from 1965 to 1977. In light of this agreement, we can state -- with a high degree of

confidence -- that there has been a moderate (15-30%) reduction in hydrocarbons and a moderate (25-35%) increase in NO_x within the Los Angeles basin from 1965 to 1977.

Historical Ozone Trends (Chapter 3)

- For the EKMA validation studies, it is desirable to use an air quality index which represents high ozone days but which has a low year-to-year meteorological variance. Unfortunately, a trade-off exists in the sense that the indices which represent the highest ozone days tend to be the least robust (statistically stable) indices. A very good compromise is the index "95th percentile of daily maximal one-hour ozone", which is used herein at the four study sites. To represent worst-case conditions, we also use the index "yearly maximum one-hour ozone" at the four study sites and for a basinwide analysis.

- Various adjustments and corrections must be applied to the historical ozone/oxidant data base in the Los Angeles area to make the data consistent for the purposes of trend analysis. Fortunately, a single monitoring technique was used during the entire study period at all but one of our 4 study sites. Thus, ozone trends at our particular study sites require relatively few adjustments and corrections.

- Ozone concentrations at Azusa, DOLA, and Anaheim decreased from the middle 1960s to the early/middle 1970s and then leveled off. All sites in Los Angeles except those in the extreme eastern parts of the basin exhibited this historical pattern in ozone trends. Similar to the trends at other sites in the far eastern part of the basin, ozone at San Bernardino increased at a very slight rate during the entire study period.

Selection of Specific Conditions for EKMA Validation (Chapter 4)

- One of the critical inputs to the EKMA isopleth model is the base period ambient 6-9 AM NMHC/NO_x ratio. Our best estimate of this

ratio for the 1964-1966 base period in Los Angeles is 13:1. This estimate is derived by examining data from several monitoring programs during the early 1970s and by extrapolating back to 1964-1966 based on historical trends in ambient precursor levels. In an attempt to make atmospheric NMHC concentrations more nearly equivalent to EKMA NMHC concentrations, the ambient NMHC data are adjusted to correspond to measurements made with propane calibration; the contributions from the nearly nonreactive compounds ethane and propane are also subtracted from the ambient NMHC data. Because of disagreements among various monitoring programs concerning the NMHC/NO_x ratio, because of uncertainties in some of the adjustments applied to the data, and because of stochastic day-to-day fluctuations in the ratio, there is considerable potential for error in our estimate of the NMHC/NO_x ratio. In sensitivity studies, we consider a range of the ratio from 7:1 to 25:1.

- The EKMA simulation conditions chosen for this study are the standard conditions except for the inclusion of post 8 AM emissions and the use of a special dilution pattern. For the studies at individual monitoring sites, we also use isopleths representing ozone at fixed irradiation times rather than maximum ozone over the entire irradiation period. A sensitivity analysis using six types of EKMA isopleths indicates that predicted ozone trends are moderately sensitive to the specific simulation conditions. In particular, the addition of post 8 AM emissions to the model significantly improves the agreement between predicted and actual ozone trends in Los Angeles.

- For the specific EKMA simulation conditions we are using, and for the type [illegible]orical precursor changes we are examining (decreasing NMHC [illegible]ncreasing NO_x), predicted ozone trends are extremely sensitive to the base period NMHC/NO_x ratio. In fact, it is obvious that potential errors in the NMHC/NO_x ratio could alone account for any of the discrepancies between predicted ozone trends

and actual ozone trends. Bearing this conclusion in mind, it is decided to conduct the EKMA validation studies under a very stringent set of test conditions (not allowing for potential errors in the NMHC/NO_x ratio).

Validation of the EKMA Isopleth Method (Chapter 5)

- In the validation studies, historical precursor trends (either emission trends or ambient precursor trends) and the EKMA isopleth model are used to predict historical ozone trends; these predicted ozone trends are then compared to actual ozone trends. Error bars representing the error in historical precursor trends are included on the predicted ozone trends; error bars representing meteorological fluctuations are included on the actual ozone trends. The validation studies are conducted for basinwide maximum ozone as well as for two ozone air quality indices at the four individual study sites.

- The results of the EKMA validation studies are nearly the same whether one uses emission trends or ambient precursor trends to derive predicted ozone trends. In both cases, the results of the validation studies are not poor considering the stringency of the test conditions (in the sense that potential errors in the NMHC/NO_x ratio are not included). For most sites and years, the predicted and actual ozone trends agree within the error bars representing variance in precursor trends and meteorological fluctuations in ozone trends. There is, however, a disturbing general tendency for predicted ozone trends to underestimate decreases in actual ozone trends at all sites except San Bernardino. This discrepancy is rather large for certain sites and years.

- We are able to eliminate three possible explanations for the observed discrepancy that predicted ozone levels tend to underestimate historical improvements in actual ozone levels. The cause is <u>not</u> errors in the historical precursor trends, because the error

bars on precursor trends are rather small, and because the precursor trends are confirmed by two independent data bases (emissions data and ambient data). Studies of met-adjusted ozone data strongly suggest that the discrepancy is also not due to meteorological fluctuations in actual ozone trends. Also, further refinements in the EKMA simulation conditions (improved dilution patterns, improved estimates of post 8 AM emissions, addition of carry-over ozone, etc.) will probably not eliminate the discrepancy because our predicted ozone trends are not quite sensitive enough to changes in the simulation conditions.

- The obvious factor that can account for observed discrepancies between predicted and actual ozone trends is error in the NMHC/NO_x ratio. We find that using a 10:1 ratio rather than a 13:1 ratio would eliminate all of the discrepancies. There are two ways in which the NMHC/NO_x ratio could be in error. First, we could be dealing with a random error in our estimate of the ratio -- an error that would not necessarily reproduce itself in applying EKMA to other areas. Second, there could be a systematic error in the EKMA chemical-kinetic mechanism or in matching the atmospheric NMHC/NO_x ratio with the EKMA NMHC/NO_x ratio. Further research should be conducted to test the EKMA kinetic mechanism and to check the equivalency between atmospheric and EKMA NMHC/NO_x ratios. This research might lead to improvements in the EKMA chemical mechanism or to guidelines for adjusting atmospheric NMHC/NO_x ratios before they are used in EKMA.

- This study has pointed out two potentially significant sensitivities of the EKMA isopleth method. The predictions of EKMA can be moderately sensitive to the specific EKMA simulation conditions and can be very sensitive to the NMHC/NO_x ratio. Thus, it may be important, in some applications, to insure that the most realistic, area-specific EKMA simulation conditions are used. Also, it may be critical to obtain an accurate estimate of the EKMA-equivalent NMHC/NO_x

ratio. Fortunately, predictions of future ozone trends are likely to be less sensitive to the simulation conditions and to the NMHC/NO_x ratio because future emission changes are likely to involve reductions in both NMHC and NO_x, and because the predictions of EKMA are much less sensitive to the simulation conditions and the NMHC/NO_x ratio when both precursors undergo similar changes.

- As a postscript to this study we consider the controversy surrounding the lack of improvement in Los Angeles ozone since the middle 1970s. Several possible explanations for this lack of improvement are considered: source growth, failure of catalytic converters, meteorological fluctuations, reversal in the historical trend of a decreasing NMHC/NO_x ratio, and overall failure of control programs. We find that source growth and catalyst failures do not appear to be reasonable explanations in light of available data. The other potential explanations seem reasonable to a degree, but each also appears to contradict certain observations. New data must be taken and more analyses must be conducted before this controversy can be resolved.

CHAPTER 2

HISTORICAL PRECURSOR TRENDS

In order to predict historical ozone trends using the EKMA method, information is needed regarding historical precursor trends. This chapter presents a comprehensive analysis of available information concerning hydrocarbon and nitrogen oxide trends in the Los Angeles basin for the period 1965 to 1977. Separate analyses are performed using emissions data and ambient precursor data; the precursor trends are examined for the entire basin as well as for various subareas of the basin. Comparisons are also made between the emission trend data and the ambient precursor trend data.

HISTORICAL EMISSION TRENDS

One of the most difficult and time-consuming tasks in this study was the compilation of historical emission trends for hydrocarbons and nitrogen oxides. Year-by-year emissions from 1965 to 1978* were estimated for various source categories using the latest information available from research firms, trade associations, and numerous federal/state/local government agencies. Appendix A provides a detailed discussion of the data, assumptions, and methodology underlying our emission trend estimates. A very brief explanation of the methodology and data sources is presented in the subsequent four paragraphs.

Fleet-averaged emission factors for each year and for each motor vehicle type (light-duty passenger cars, light-duty trucks, medium-duty trucks, heavy-duty gasoline trucks, heavy-duty diesel trucks, and motorcycles) were provided by the EPA Ann Arbor Laboratory using a recent version of the MOBILE2 computer program (Platte 1980; Wallis 1980). The latest California-specific version of MOBILE2 contains very substantial improvements over previous MOBILE1 programs for California (EPA 1978b;

*Although the EKMA validation study will only use emission trend data through 1977, we found it convenient to include 1978 in our emission trend analysis.

ARB 1980a). The MOBILE2 program was run with speed distributions, age/mileage distributions, hot/cold start mixes, and temperature/humidity corrections specific to Los Angeles. Total emission trends for each type of motor vehicle were obtained by combining the fleet-averaged emission factors with Los Angeles specific data regarding traffic growth and the distribution of traffic by vehicle type (LARTS 1971, 1979, 1980; SCAG 1980).

Base year emissions for non-vehicular mobile sources (aircraft, ships, and railroads) were obtained from two reports by TRW Inc. (Trijonis et al. 1975; Trijonis and Arledge 1976). These emissions were projected backward and forward in time using information on source growth and control levels obtained from the California Air Resources Board (ARB), Southern California Air Quality Management District (SCAQMD), Federal Aviation Administration, American Association of Railroads, U.S. Department of Commerce, and various research publications.

Base year emissions for stationary sources of hydrocarbons and nitrogen oxides were obtained from two comprehensive stationary source inventories compiled by KVB Engineering (Bartz et al. 1976; Taback et al. 1978). Data on growth for various stationary source categories came from the ARB, SCAQMD, California Energy Commission, U.S. Department of Commerce, and research publications. Most of the information on historical control levels for stationary sources was obtained through contacts with the ARB and SCAQMD.

It should be noted that the hydrocarbon emission trends compiled herein refer to reactive hydrocarbons (RHC). Estimates of RHC emissions were derived from data on total hydrocarbon emissions using a two-group reactivity classification scheme proposed by Dimitriades (1974), with reactivity ratings specific to Los Angeles source categories calculated by Trijonis and Arledge (1976).

Basinwide Emission Trends

Figures 1 and 2 summarize basinwide emission trends for RHC and NO_x on a yearly basis from 1965 to 1978. The top line in each figure represents total emission trends, while the distances between lines represent contributions from individual source categories. The points for 1978 are

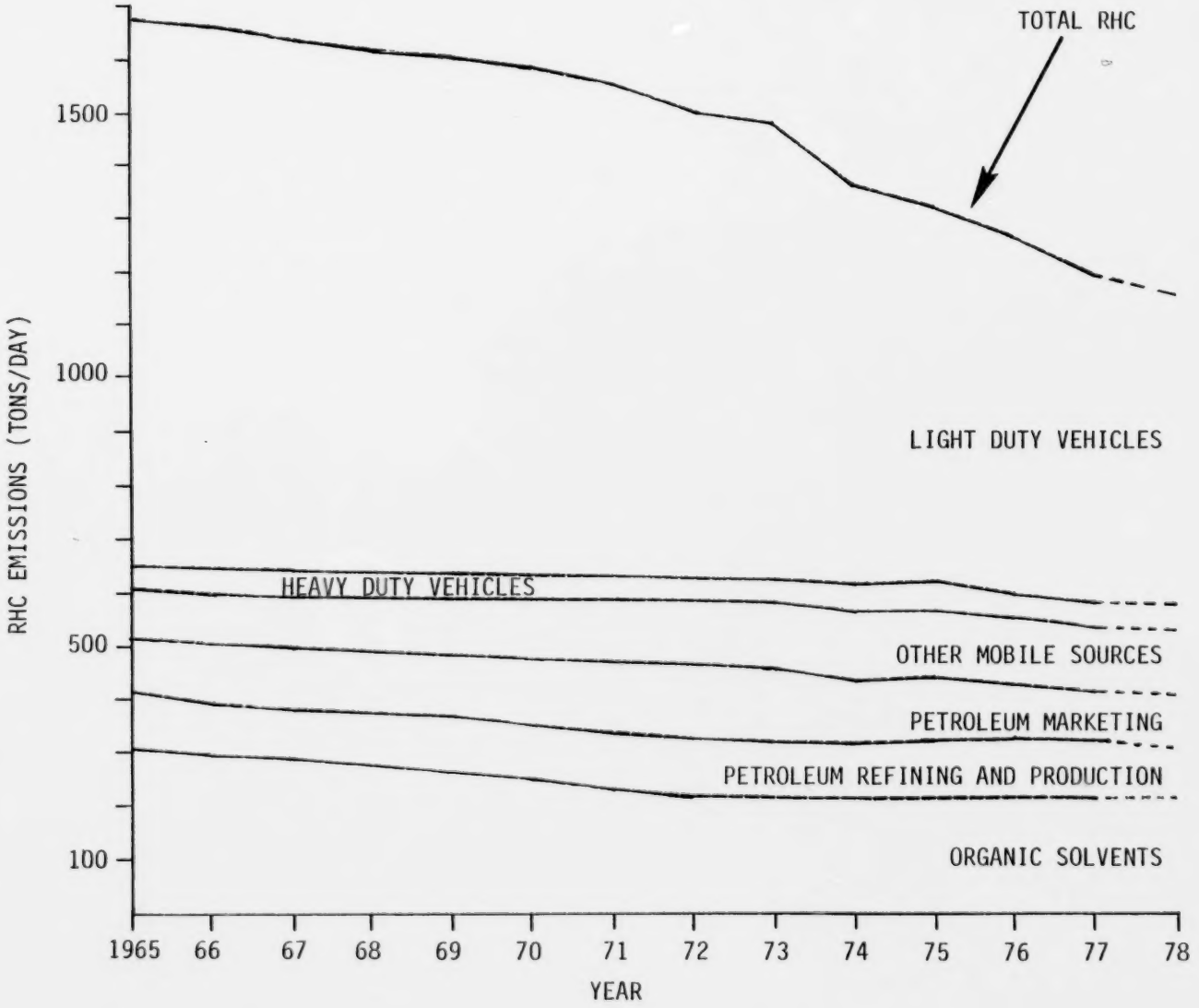

Figure 1. Historical RHC emission trends in the Los Angeles basin.

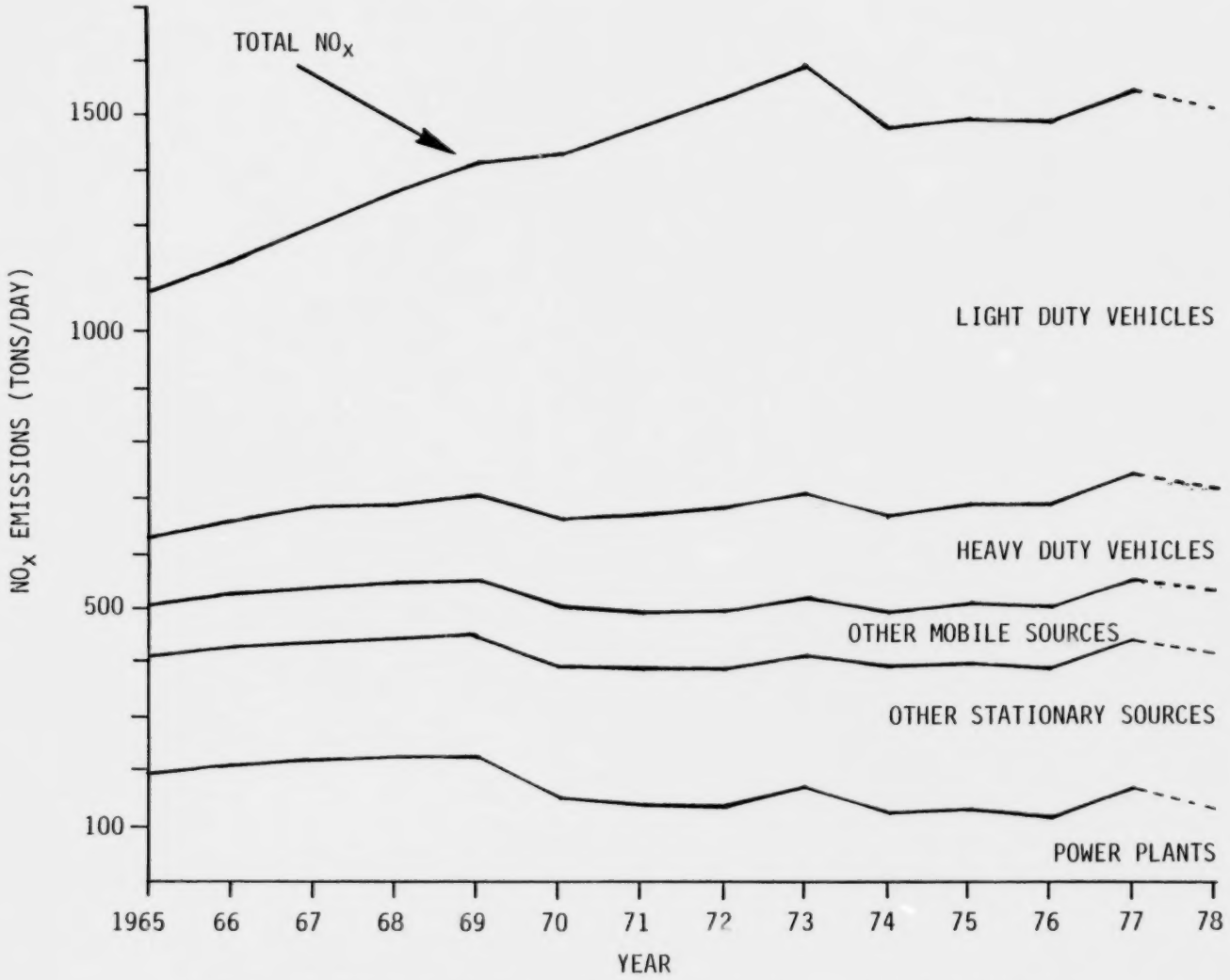

Figure 2. Historical NO_X emission trends in the Los Angeles basin.

connected with dashed lines because only data for 1965 to 1977 are required for the EKMA validation study.

Figure 1 includes six major source categories of RHC: organic solvents* (surface coating, dry cleaning, degreasing, printing, domestic/industrial solvent use, etc.), petroleum refining/production, petroleum marketing, light-duty vehicles (passenger cars, light-duty trucks, and medium-duty trucks), heavy-duty vehicles (both gas and diesel), and other mobile sources (motorcycles, aircraft, ships, and trains). The dominant source category is light-duty vehicles which accounted for 61% of total RHC emissions in 1965 and 52% in 1977.

As illustrated in Figure 1, basinwide RHC emissions decreased continually throughout the study period. The net decrease from 1965 to 1977 was 29%, with the predominant part of this decrease coming from a 40% decrease in light-duty vehicle emissions (see Table 1).

TABLE 1. RHC EMISSION CHANGES IN THE LOS ANGELES BASIN FROM 1965 TO 1977.

SOURCE CATEGORY	1965 EMISSIONS (tons/day)	1977 EMISSIONS (tons/day)	1965 TO 1977 EMISSION CHANGE Absolute	Percent
Light-Duty Vehicles	1025	619	-406	-40%
Heavy-Duty Vehicles	46	42	- 4	- 9%
Other Mobile Sources	95	126	+ 31	+33%
Petroleum Marketing	104	97	- 7	- 7%
Petroleum Production/Refining	102	102	0	0%
Organic Solvents	305	212	- 93	-30%
Total	1677	1198	-479	-29%

*The extremely small contribution from miscellaneous stationary area sources has been included in this source category.

The 40% decrease in RHC emissions from light-duty vehicles was attained despite a 54% increase in traffic from 1965 to 1977. Fleet-averaged RHC emission factors for light-duty vehicles decreased 61% from 1965 to 1977. The reduction in light-duty vehicle emissions was, of course, due to the California/federal motor vehicle controls (crankcase controls in the early/middle 1960s, ever-tightening exhaust controls starting in 1966, and evaporative controls beginning in 1970). Actually, the reduction in RHC emissions from light-duty vehicles could have been even greater were it not for deterioration of exhaust control systems and problems with the first few years of evaporative controls.

As shown in Table 1, the only other source category that produced a significant reduction in RHC emissions was organic solvents. Organic solvent emissions decreased 30% from 1965 to 1977, with the reduction basically occurring between 1965 and 1974. Emissions from heavy duty vehicles and petroleum marketing decreased 9% and 7%, respectively, from 1965 to 1977 as the controls on these sources barely outstripped growth in traffic and gasoline sales.* Emissions from petroleum production/refining remained constant over the period. Emissions from the "other mobile sources" category increased 33%.

Figure 2 includes five major source categories for NO_x: electric power plants, other stationary sources (basically residential/commercial/industrial fuel combustion), light-duty vehicles, heavy-duty vehicles, and other mobile sources. Again, the largest single source category is light-duty vehicles which accounted for 42% of total NO_x emissions in 1965 and 48% in 1977.

As shown in Figure 2, total NO_x emissions increased rapidly from 1965 to 1973 and then basically levelled off. The unusual downward jump from 1973 to 1974 was due to the gasoline crisis of 1974 and to reduced power plant emissions during 1974. Over the entire study period, 1965 to 1977, basinwide NO_x emissions increased 34%. The predominant part of this rise

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*Filling of underground service station tanks was controlled by submerged fill in 1965 and balanced fill in 1976. Controls on auto tank filling did not start until 1979.

was due to light-duty vehicles which increased in NO_x emissions by 55% from 1965 to 1977 (see Table 2).

TABLE 2. NO_x EMISSION CHANGES IN THE LOS ANGELES BASIN FROM 1965 TO 1977.

SOURCE CATEGORY	1965 EMISSIONS (tons/day)	1977 EMISSIONS (tons/day)	1965 TO 1977 EMISSION CHANGE Absolute	Percent
Light-Duty Vehicles	453	700	+247	+55%
Heavy-Duty Vehicles	123	190	+ 67	+54%
Other Mobile Sources	96	113	+ 17	+18%
Power Plants	197	170	- 27	-14%
Other Stationary Sources	211	278	+ 67	+32%
Total	1080	1451	+371	+34%

The 55% increase in light-duty vehicle NO_x from 1965 to 1977 was mostly due to a 52% rise in traffic; fleet-averaged NO_x emission factors increased only 1% from 1965 to 1977. During the initial part of the study period, 1965 to 1973, there was an even greater increase in vehicular NO_x emissions (74%) due to traffic growth and the fact that the control techniques for RHC and CO emissions in 1966-1969 model year vehicles had the side effect of raising NO_x emissions. New car emission standards for NO_x did not start until 1971, and it was not until 1973 that these standards started to produce a gradual decline in total light-duty vehicle NO_x emissions.

As shown in Table 2, NO_x emissions from heavy-duty vehicles increased 54% from 1965 to 1977, basically reflecting growth in traffic (although there were some very minor changes in vehicle emission factors). NO_x emissions from other mobile sources (motorcycles, ships, and trains) increased 18% over the study period. Power plant NO_x emissions -- affected by partial NO_x controls in the late 1960s and early 1970s, by load changes, and by shifts in fuel types -- decreased 14% from 1965 to 1977. NO_x emissions from

other stationary sources increased 32%, basically reflecting growth in natural gas usage in the residential/commercial/industrial sectors.

Emission Trends For Various Source Areas

As noted in Chapter 1, the EKMA validation study will be conducted using basinwide ozone trends as well as ozone trends at four individual monitoring sites: Azusa, DOLA, Anaheim, and San Bernardino. The emission trends relevant to the validation study are the emission trends for the specific source areas that affect basinwide maximum ozone as well as ozone at the four individual sites. The selection of appropriate source areas has been extensively discussed in previous reports (Trijonis and Hunsaker 1978; Eldon and Trijonis 1977). Those studies defined source areas based on an analysis of numerous wind trajectory/wind streamline studies representing typical conditions during the Los Angeles smog season and ozone episode conditions. Figures 3 through 6 illustrate the source areas responsible for high ozone concentrations at Azusa, DOLA, Anaheim, and San Bernardino, respectively. The source area for basinwide maximum ozone is the same as the Azusa source area (Figure 3).

Data on historical source growth rates (e.g. traffic growth rates) are not available with sufficient spatial detail to conduct a rigorous, quantitative analysis of emission trends for the individual source areas. To estimate emission trends for the individual source areas, we made approximate adjustments to the basinwide emission trends, taking into account the detailed spatial distribution of population growth in the Los Angeles region (Trijonis and Hunsaker 1978), the county-by-county distribution of traffic growth (Trijonis et al. 1978), and the spatial distribution of various source types (Trijonis et al. 1975; ARB 1980b). The resulting estimates of emission trends for the various source areas are listed in Table 3. The trends are specified in terms of the net percent change in emissions from the base period (1964-1966) to each subsequent 3-year period.*

*As noted in Chapter 1, the EKMA validation study will use 1964-1966 as a base period, with prediction of ozone levels being made for each subsequent 3-year period.

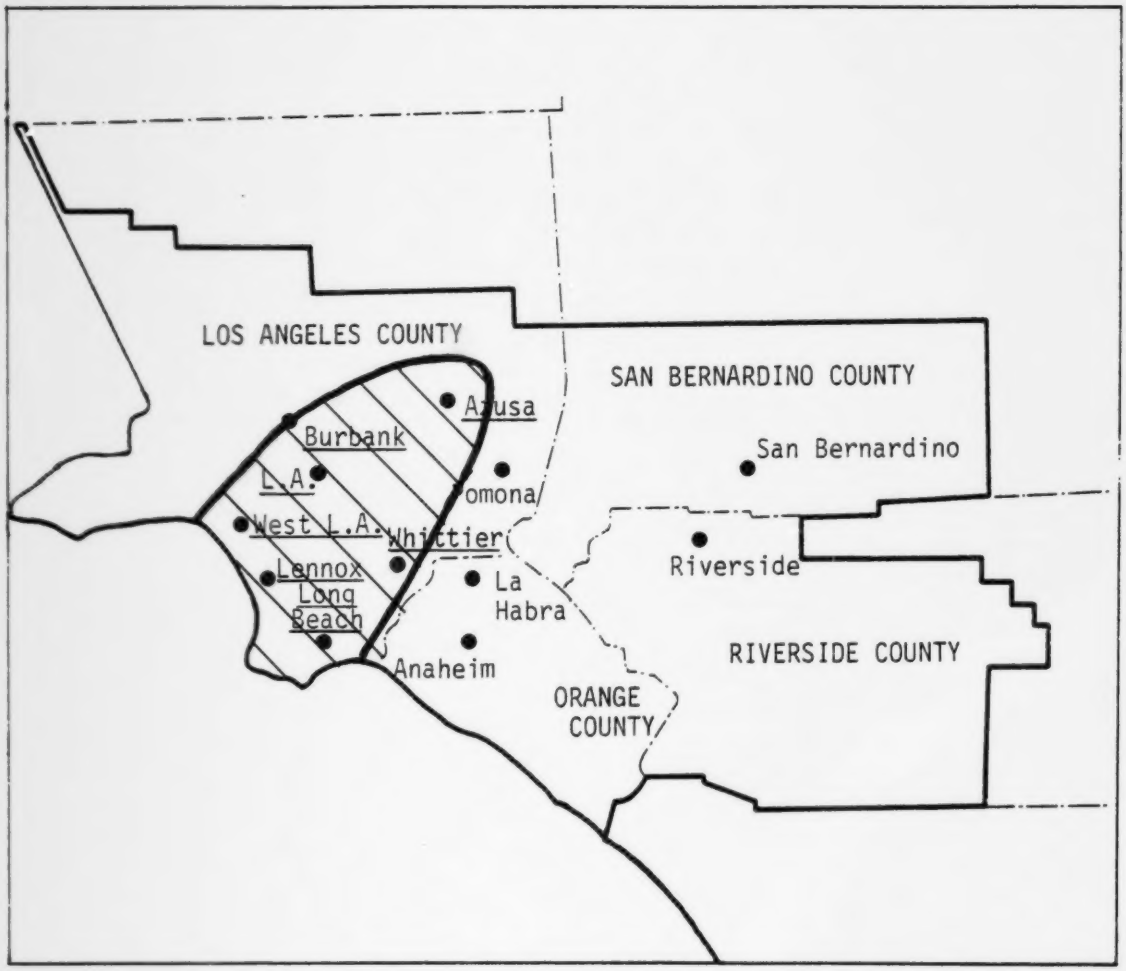

Figure 3. Approximate source area affecting ozone at Azusa.

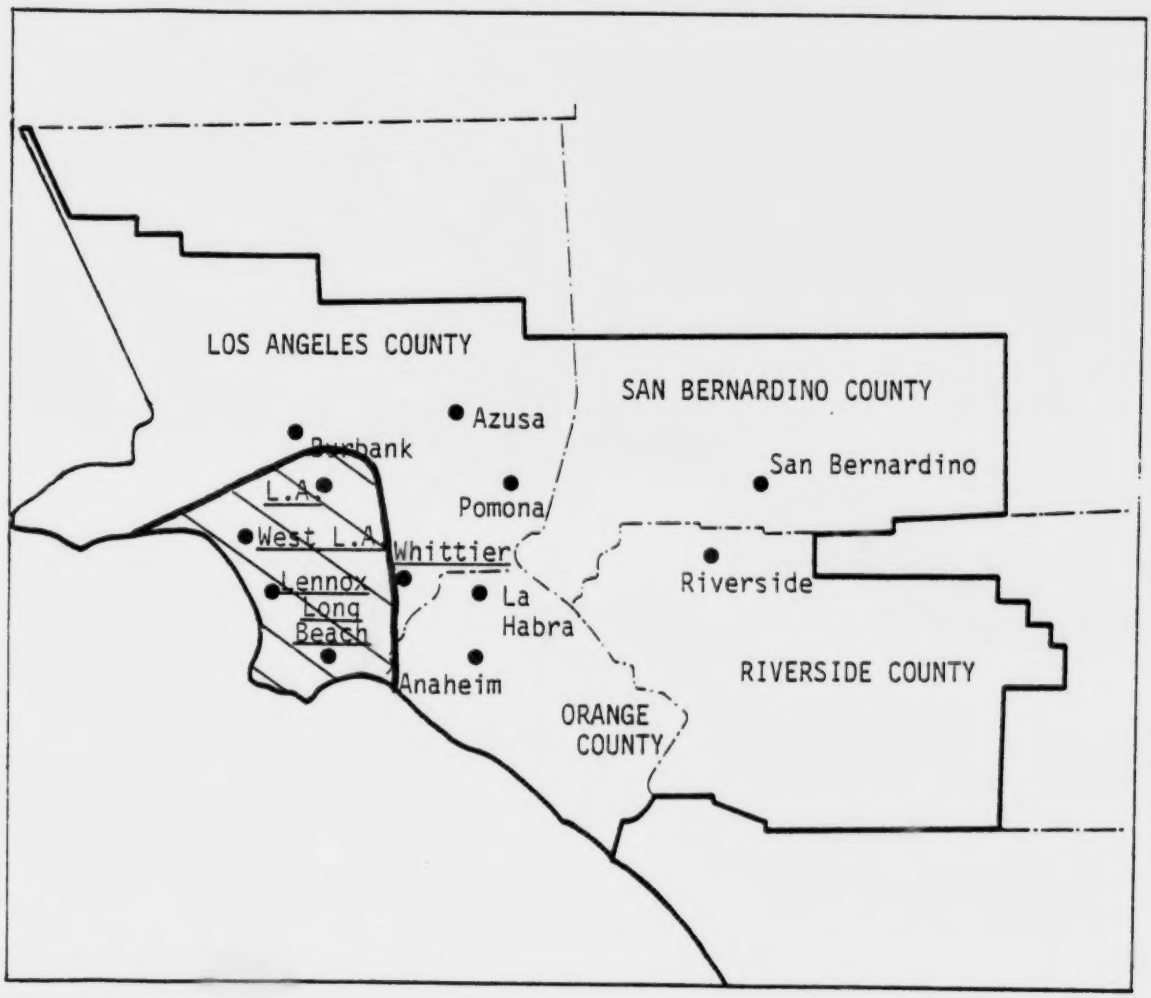

Figure 4. Approximate source area affecting ozone at Downtown Los Angeles.

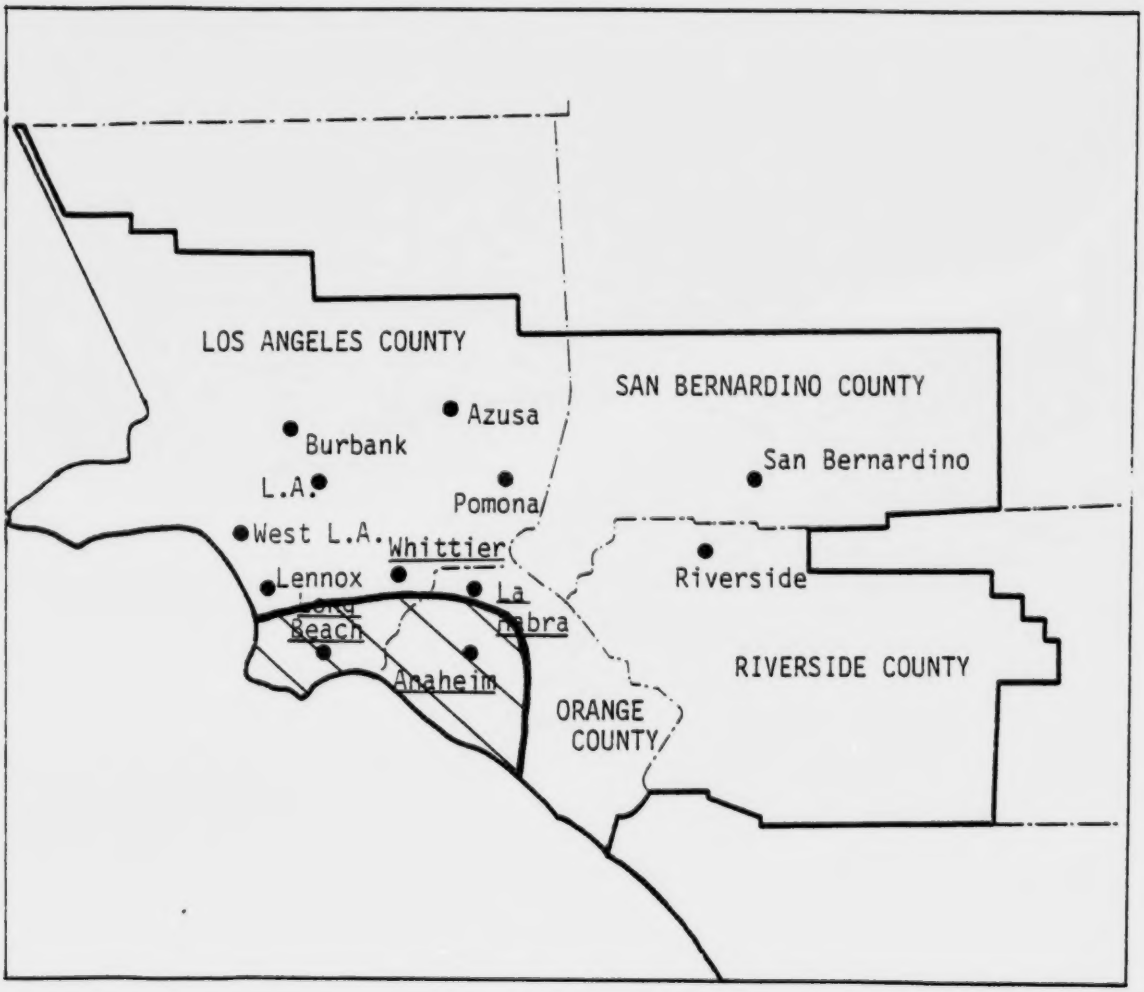

Figure 5. Approximate source area affecting ozone at Anaheim.

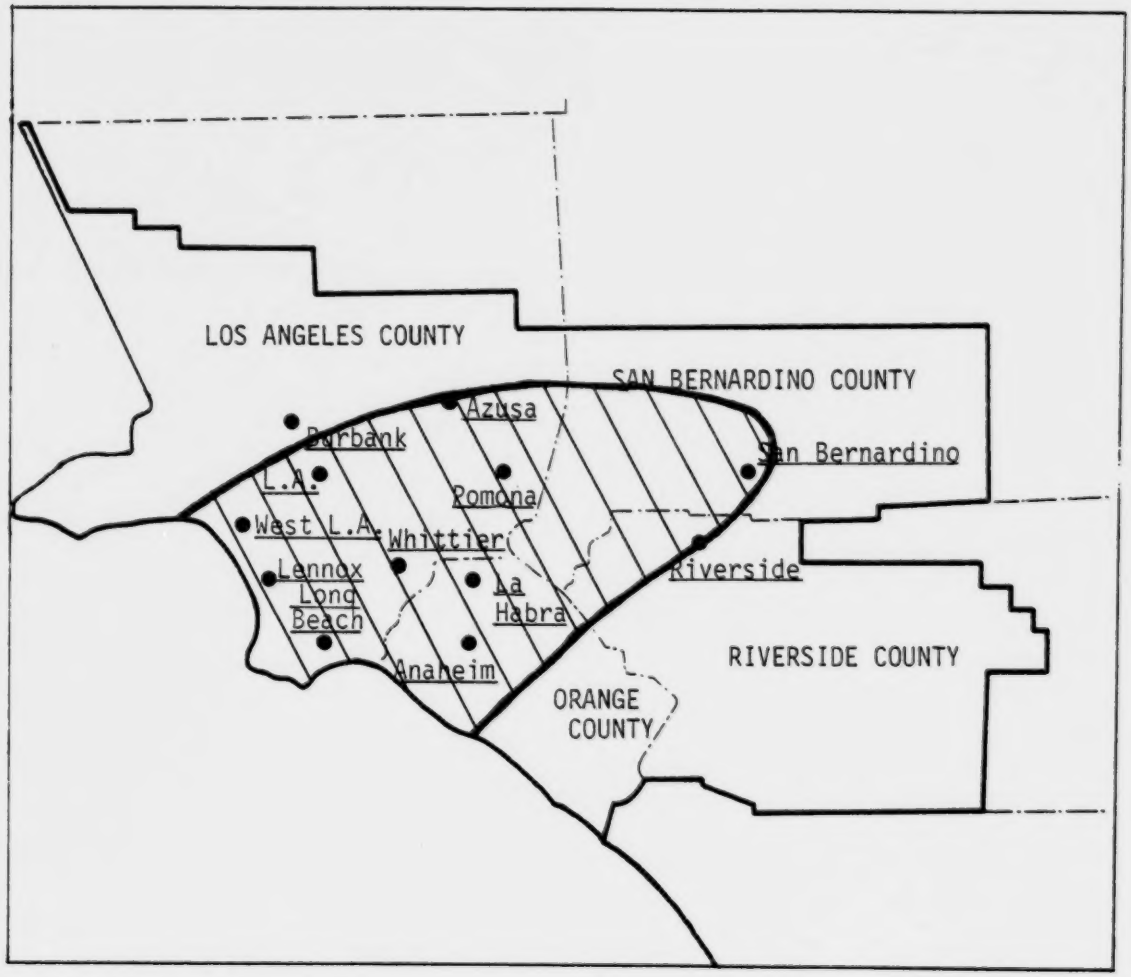

Figure 6. Approximate source area affecting ozone at San Bernardino.

Table 3 also presents error bounds on the emission trend estimates. These error bounds are based on our subjective evaluation of the uncertainties in the basinwide emission trends as well as the uncertainties in estimating emission trends for individual source areas from the basinwide results. The error bounds increase with time because some of the uncertainties are compounded over time.

TABLE 3. ESTIMATES OF EMISSION TRENDS FOR INDIVIDUAL SOURCE AREAS.

Table 3a. RHC Emission Trends.

↓ Years/Source Area →	Azusa	DOLA	Anaheim	San Bernardino
1964-1966	0%	0%	0%	0%
1967-1969	- 5% ± 4%	- 5% ± 4%	- 2% ± 4%	- 4% ± 3%
1970-1972	-11% ± 6%	-12% ± 6%	- 4% ± 6%	- 9% ± 5%
1973-1975	-24% ± 10%	-26% ± 10%	-12% ± 10%	-20% ± 8%
1976-1978	-34% ± 12%	-36% ± 12%	-19% ± 12%	-30% ± 10%

Table 3b. NO_x Emission Trends.

↓ Years/Source Area →	Azusa	DOLA	Anaheim	San Bernardino
1964-1966	0%	0%	0%	0%
1967-1969	+15% ± 7%	+13% ± 6%	+23% ± 8%	+17% ± 6%
1970-1972	+21% ± 10%	+18% ± 9%	+36% ± 11%	+27% ± 9%
1973-1975	+22% ± 11%	+18% ± 10%	+43% ± 13%	+31% ± 10%
1976-1978	+20% ± 12%	+16% ± 11%	+43% ± 14%	+29% ± 11%

AMBIENT PRECURSOR TRENDS

A second method for investigating historical changes in precursor levels is to examine ambient trend data for NMHC and NO_x. Figure 7 illustrates the monitoring sites in our study area that provide long-term trend data for hydrocarbons and/or NO_x. An "H" in Figure 7 denotes hydrocarbon trend data, while an "N" denotes NO_x trend data.

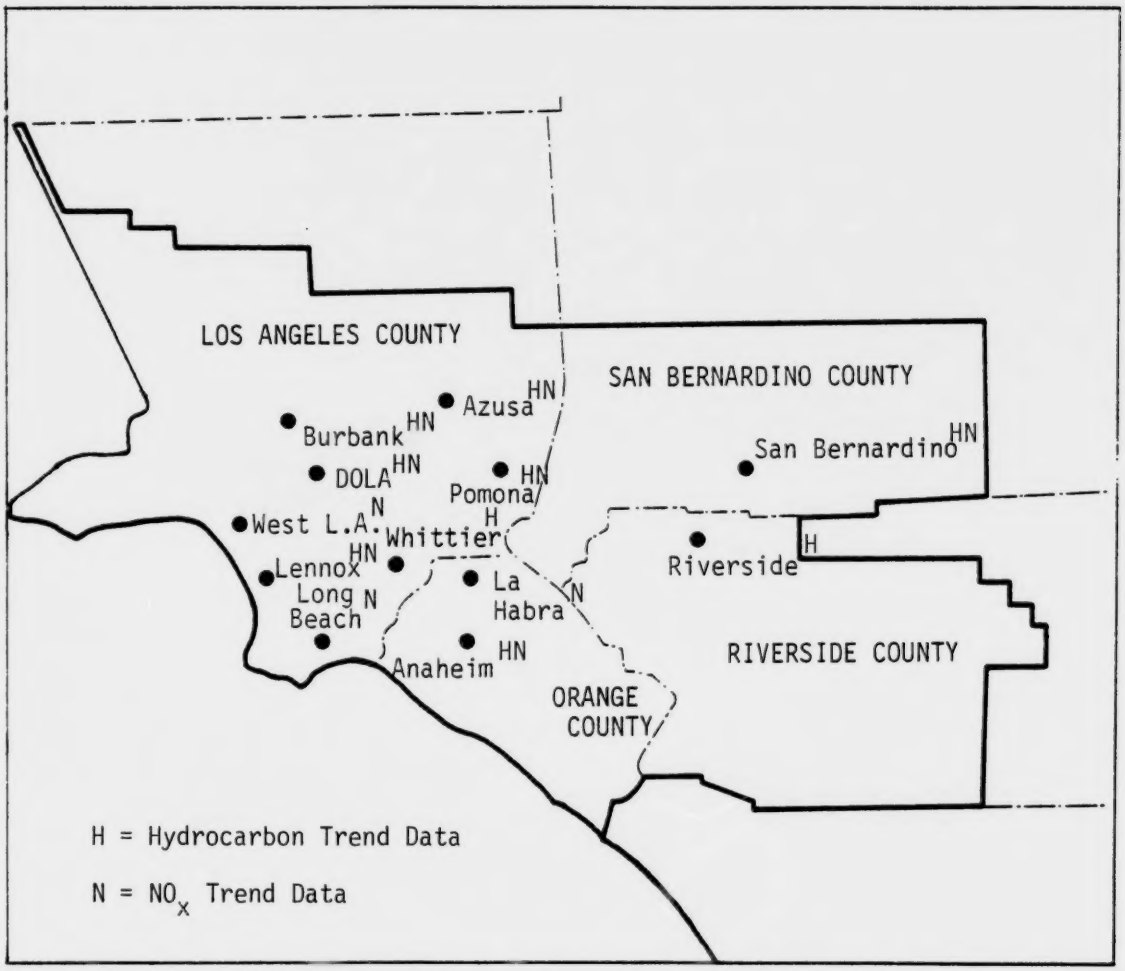

Figure 7. Monitoring sites used to characterize ambient precursor trends in the Los Angeles basin.

Adjustments and Corrections to the Ambient Precursor Trend Data

It should be noted that the ambient precursor trend data used herein have been subjected to several adjustment procedures discussed by Trijonis (1980). These adjustments are as follows:

- NMHC trends are computed from total hydrocarbon (THC) data using an empirical formula developed by Paskind and Kinosian (1974). This formula is NMHC = 0.6(THC - 1.5), with units of ppmC.
- In order to account for a switch from propane to methane calibration in the middle 1970s, pre-1975 Orange County THC, pre-1975 Riverside County THC, and pre-1977 San Bernardino County THC are multiplied by a factor of 0.70.
- To adjust for relocation of the Riverside monitoring site in 1972, post-1972 THC data at Riverside are multiplied by a factor of 0.75.

Additionally, interpolations or extrapolations have been made in the trends at certain sites with missing or incomplete years of data. The interpolated years are based on data for the specific site in question, while extrapolations to end years with missing data are based on trends at nearby locations. Most of the extrapolations are minor; the only three major extrapolations involve the hydrocarbon trends at Lennox, Whittier, and Pomona. Ambient hydrocarbon trend data for these sites begin in 1970; these data are extrapolated back to 1964 by using DOLA for Lennox, DOLA and Anaheim for Whittier, and Azusa and San Bernardino for Pomona. We think it is useful to include Lennox, Whittier, and Pomona because these sites help to confirm hydrocarbon trends from 1970 to 1978.

Selection of an Air Quality Index

Our analysis of ambient NMHC and NO_x trends is based on a single air quality index -- the yearly average of daily maximum hourly concentrations (average daily maximum). It is much easier to compile trends for this index than other indices because of published reports for this air quality index (ARB 1974, 1977, 1976-78). Trijonis and Hunsaker (1978) and Trijonis (1980)

have shown that the average daily maximum index yields trends that are nearly identical with trends in annual mean concentrations for the precursors. Trijonis and Hunsaker have also shown that, in the case of hydrocarbons, the trends for the average daily maximum are nearly identical to trends for average 6-9 AM summertime concentrations. However, trends for average daily maximum NO_x slightly underestimate historical increases in average 6-9 AM summertime NO_x concentrations. A rudimentary sensitivity analysis indicates that the latter discrepancy should not be important to the results of this study.

Precursor Trend Data and Error Bars

As discussed previously, we are interested in precursor trends for the four source areas illustrated in Figures 3 to 6. Those figures indicate, by underlining, the stations used to determine ambient precursor trends in each source area. In a few cases, monitoring stations that border the source area, but are not inside the source area, have been included in order to provide more robust data on precursor trends.

Tables 4 through 7 summarize ambient precursor trends for the four source areas. The precursor trends are expressed as net percent changes in (average daily maximum) concentrations at each monitoring site from 1964-66 to subsequent three-year periods. The average (over the monitoring sites) of these percent changes will be used to represent the ambient precursor trends for the entire source area.*

*An alternative way of calculating ambient precursor trends for each source area would be to use the percent change of the average concentration among the sites (rather than the average of the percent changes). We have performed this alternative calculation for each source area and each set of years. The alternative averaging method generally yields about 1 to 7% greater NMHC decreases and 1 to 7% less NO_x increases than our original method, depending on the source area and years. This outcome makes sense because the alternative method emphasizes the sites with the highest concentrations, which are the sites in the most dense emission areas, which in turn are the lowest growth areas. We decided to stay with our original method because we thought that the high concentration (low growth) areas were already emphasized by viture of the greater densities of monitoring sites in those areas. In any case, the results of the alternative averaging method are only slightly different from the results of our original method; the choice of an averaging technique has negligible influence on the EKMA validation tests.

TABLE 4. AMBIENT PRECURSOR TRENDS FOR THE SOURCE AREA AFFECTING AZUSA OZONE.

Table 4.a. Percent Changes in Yearly Average of Daily One-Hour Maximum NMHC Relative to 1964 - 1966.

YEAR	STATION					AVERAGE OF PERCENT CHANGES	ERRORS		
	DOLA	LENNOX	WHITTIER	BURBANK	AZUSA		Station Representativeness E_1	Meteorological Variance E_2	Total Error $\sqrt{E_1^2 + E_2^2}$
1964 - 66	0%	0%	0%	0%	0%	0%	-	-	-
1967 - 69	-25%	-25%	-17%	+ 8%	+17%	- 8%	10%*	7%	12%
1970 - 72	-25%	-25%	-13%	+11%	+51%	0%	16%*	7%	17%
1973 - 75	-49%	-43%	-36%	- 8%	+21%	-23%	13%	7%	15%
1976 - 78	-42%	-28%	- 3%	- 1%	+ 6%	-14%	9%	7%	11%

Table 4.b. Percent Changes in Yearly Average of Daily One-Hour Maximum NO_x Relative to 1964 - 1966.

YEAR	STATION						AVERAGE OF PERCENT CHANGES	ERRORS		
	DOLA	LENNOX	BURBANK	AZUSA	LONG BEACH	WEST L.A.		Station Representativeness E_1	Meteorological Variance E_2	Total Error $\sqrt{E_1^2 + E_2^2}$
1964 - 66	0%	0%	0%	0%	0%	0%	0%	-	-	-
1967 - 69	+ 7%	+25%	+34%	+16%	+19%	+ 8%	+18%	4%	7%	8%
1970 - 72	+22%	+33%	+36%	+56%	+20%	+17%	+31%	6%	7%	9%
1973 - 75	0%	+16%	+ 7%	+47%	- 8%	+10%	+12%	8%	7%	11%
1976 - 78	+14%	+22%	+19%	+63%	0%	+13%	+22%	9%	7%	11%

* In calculating this standard deviation, the number of degrees of freedom has been reduced by 1 because there are only 4 (not 5) independent sites for determining trends during this period.

TABLE 5. AMBIENT PRECURSOR TRENDS FOR THE SOURCE AREA AFFECTING DOWNTOWN LOS ANGELES OZONE.

Table 5.a. Percent Changes in Yearly Average of Daily One-Hour Maximum NMHC Relative to 1964 - 1966.

YEAR	STATION			AVERAGE OF PERCENT CHANGES	ERRORS		
	DOWNTOWN LOS ANGELES	LENNOX	WHITTIER		Station Representativeness E_1	Meteorological Variance E_2	Total Error $\sqrt{E_1^2 + E_2^2}$
1964 - 66	0%	0%	0%	0%	-	-	-
1967 - 69	-25%	-25%	-17%	-22%	3%*	7%	8%
1970 - 72	-25%	-25%	-13%	-21%	5%*	7%	9%
1973 - 75	-49%	-43%	-36%	-43%	4%	7%	8%
1976 - 78	-42%	-28%	- 3%	-24%	11%	7%	13%

Table 5.b. Percent Changes in Yearly Average of Daily One-Hour Maximum NO_x Relative to 1964 - 1966.

YEAR	STATION				AVERAGE OF PERCENT CHANGES	ERRORS		
	DOWNTOWN LOS ANGELES	LENNOX	WEST L.A.	LONG BEACH		Station Representativeness E_1	Meteorological Variance E_2	Total Error $\sqrt{E_1^2 + E_2^2}$
1964 - 66	0%	0%	0%	0%	0%	-	-	-
1967 - 69	+ 7%	+25%	+ 8%	+19%	+15%	4%	7%	8%
1970 - 72	+22%	+33%	+17%	+20%	+23%	3%	7%	8%
1973 - 75	0%	+16%	+10%	- 8%	+ 5%	5%	7%	9%
1976 - 78	+14%	+22%	+13%	0%	+12%	5%	7%	9%

* In calculating this standard deviation, the number of degrees of freedom has been reduced by 1 because there are only 2 (not 3) independent sites for determining trends during this period.

TABLE 6. AMBIENT PRECURSOR TRENDS FOR THE SOURCE AREA AFFECTING ANAHEIM OZONE.

Table 6.a. Percent Changes in Yearly Average of Daily One-Hour Maximum NMHC Relative to 1964 - 1966.

YEAR	STATION		AVERAGE OF PERCENT CHANGES	ERRORS		
	ANAHEIM	WHITTIER		Station Representativeness E_1	Meteorological Variance E_2	Total Error $\sqrt{E_1^2 + E_2^2}$
1964 - 66	0%	0%	0%	-	-	-
1967 - 69	- 9%	-17%	-13%	4%	7%	8%
1970 - 72	- 1%	-13%	- 7%	6%	7%	9%
1973 - 75	-10%	-36%	-23%	13%	7%	15%
1976 - 78	-33%	- 3%	-18%	15%	7%	17%

Table 6.b. Percent Changes in Yearly Average of Daily One-Hour Maximum NO_x Relative to 1964 - 1966.

YEAR	STATION			AVERAGE OF PERCENT CHANGES	ERRORS		
	ANAHEIM	LA HABRA	LONG BEACH		Station Representativeness E_1	Meteorological Variance E_2	Total Error $\sqrt{E_1^2 + E_2^2}$
1964 - 66	0%	0%	0%	0%	-	-	-
1967 - 69	+86%	+ 6%	+19%	+37%	25%	7%	26%
1970 - 72	+86%	+18%	+20%	+41%	22%	7%	23%
1973 - 75	+80%	+48%	- 8%	+40%	26%	7%	27%
1976 - 78	+91%	+41%	0%	+44%	26%	7%	27%

TABLE 7. AMBIENT PRECURSOR TRENDS FOR THE SOURCE AREA AFFECTING SAN BERNARDINO OZONE.

Table 7.a. Percent Changes in Yearly Average of Daily One-Hour Maximum NMHC Relative to 1964 - 1966.

YEAR	STATION									AVERAGE OF PERCENT CHANGES	ERRORS		
	ANA-HEIM	AZUSA	BUR-BANK	LOS ANGELES	SAN BER-NARDINO	LENNOX	WHITTIER	POMONA	RIVER-SIDE		Station Representativeness E_1	Meteorological Variance E_2	Total Error $\sqrt{E_1^2 + E_2^2}$
1964 - 66	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	-	-	-
1967 - 69	- 9%	+17%	+ 8%	-25%	+ 1%	-25%	-17%	+ 9%	-16%	- 6%	6%*	7%	9%
1970 - 72	- 1%	+51%	+11%	-25%	- 9%	-25%	-13%	+21%	-24%	- 2%	10%*	7%	12%
1973 - 75	-10%	+21%	- 8%	-49%	- 9%	-43%	-36%	+13%	-25%	-16%	8%	7%	11%
1976 - 78	-33%	+ 6%	- 1%	-42%	+ 7%	-28%	- 3%	- 1%	-28%	-14%	6%	7%	9%

Table 7.b. Percent Changes in Yearly Average of Daily One-Hour Maximum NO_x Relative to 1964 - 1966.

YEAR	STATION										AVERAGE OF PERCENT CHANGES	ERRORS		
	ANAHEIM	AZUSA	BURBANK	LA HABRA	LENNOX	LONG BEACH	LOS ANGELES	POMONA	SAN BER-NARDINO	WEST L.A.		Station Representativeness E_1	Meteorological Variance E_2	Total Error $\sqrt{E_1^2 + E_2^2}$
1964 - 66	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	-	-	-
1967 - 69	+86%	+16%	+34%	+ 6%	+25%	+19%	+ 7%	+31%	- 1%	+ 8%	+23%	8%	7%	11%
1970 - 72	+86%	+56%	+36%	+18%	+33%	+20%	+22%	+48%	+ 1%	+17%	+34%	8%	7%	11%
1973 - 75	+80%	+47%	+ 7%	+48%	+16%	- 8%	0%	+29%	+10%	+10%	+24%	9%	7%	11%
1976 - 78	+91%	+63%	+19%	+41%	+22%	0%	+14%	+34%	-40%	+13%	+26%	11%	7%	13%

* In calculating this standard deviation, the number of degrees of freedom has been reduced by 3 because there are only 6 (not 9) independent sties for determining trends during this period.

As noted in Tables 4 through 7, there are two major sources of error in the precursor trend estimates. The first error (E_1) measures the degree to which the various monitoring sites represent trends for the entire source area. This error is estimated very simply as just the standard deviation of the mean of the percent changes over the sites (which is just the standard deviation of the percent changes among the sites divided by the square root of the number of sites*).

The second error (E_2) represents the meteorological variance in the ambient trend data. Trijonis and Hunsaker (1978) and Trijonis (1980) have formulated a method of estimating year-to-year meteorological variance based on the "de-trended" standard deviation of yearly air quality values, i.e. the deviation of yearly air quality values away from a trend line during a period of approximately linear air quality trends. Applying this method to ambient precursor trends, we find that the year-to-year meteorological variance for a single monitoring station is approximately 12% for NMHC and 10% for NO_x (using the yearly average of daily maximum hourly values as the yearly air quality index). Applying this same method to groups of stations ($\sim$ 3 to 5 stations), we find that the meteorological variance is slightly less for groups of stations, approximately 8% for both NMHC and NO_x. Because Tables 2 through 8 deal with trends for groups of stations, the 8% meteorological error is relevant here. Two further adjustments, however, must be made to this error estimate. We are dealing with 3-year averages, not 1-year averages; the meteorological variance for 3-year averages should be approximately $8\%/\sqrt{3}$ or 5%. Also, we are dealing with differences between the three-year averages (e.g. between 1964-1966 and 1967-1969); the error in the difference should be $\sqrt{2}$ times the error in each number. Thus, the error of interest is $\sqrt{2} \times 5\% = 7\%$.

To obtain the total error in the ambient precursor trends due to both station representativeness errors and meteorological fluctuations, we use the routine "sum of the squares" formula. That is -- the total error is

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*In mathematical terms, if there are N data points (X_i for i - 1, ..., N) with mean $\bar{X}$ and standard deviation σ, then the error in the estimate of $\bar{X}$ is $\sigma/\sqrt{N}$.

assumed to be $E_t = \sqrt{E_1^2 + E_2^2}$. It should be remarked that this error essentially represents a single standard deviation; thus, it corresponds to a 70% confidence interval.

COMPARISON OF EMISSION TRENDS AND AMBIENT PRECURSOR TRENDS

Figures 8 and 9, for hydrocarbons and NO_x respectively, compare emission trends with ambient trends in each of the four source areas. As evidenced by these figures, the agreement between emission trends and ambient trends is generally very good, especially when the data are viewed in an overall sense from 1965 to 1977. The error bounds in the figures nearly always overlap. Also, within all four source areas, both the emission and ambient data show approximately the same overall decreases in hydrocarbons and increases in NO_x. In fact, considering the agreement between the emissions and ambient data, we certainly can state -- with a high degree of confidence -- that there has been a moderate decrease in hydrocarbons and a moderate increase in NO_x within the Los Angeles basin from 1965 to 1977. In particular, examining the trends for the San Bernardino source area which includes nearly all the emissions in the basin and nearly all the monitoring sites, it appears that NMHC (or RHC) levels basinwide have decreased 15-30% from 1965 to 1977 while NO_x levels basinwide have increased 25-35%.

Another significant feature of Figures 8 and 9 is that the agreement between emissions and ambient trends is somewhat better for NO_x than it is for hydrocarbons. This makes good sense. The ambient trend data are better for NO_x because NO_x monitoring instruments are more reliable than NMHC monitoring instruments (Eldon and Trijonis 1977), and because there are more trend monitoring sites for NO_x than for NMHC. Furthermore, the stationary source emission trend data should be more accurate for NO_x than for RHC. For NO_x, there are only two significant stationary source categories (power plants and natural gas usage in the residential/commercial/industrial sectors), and historical growth/control levels for these categories can be documented rather accurately. For RHC, there are numerous individual types of

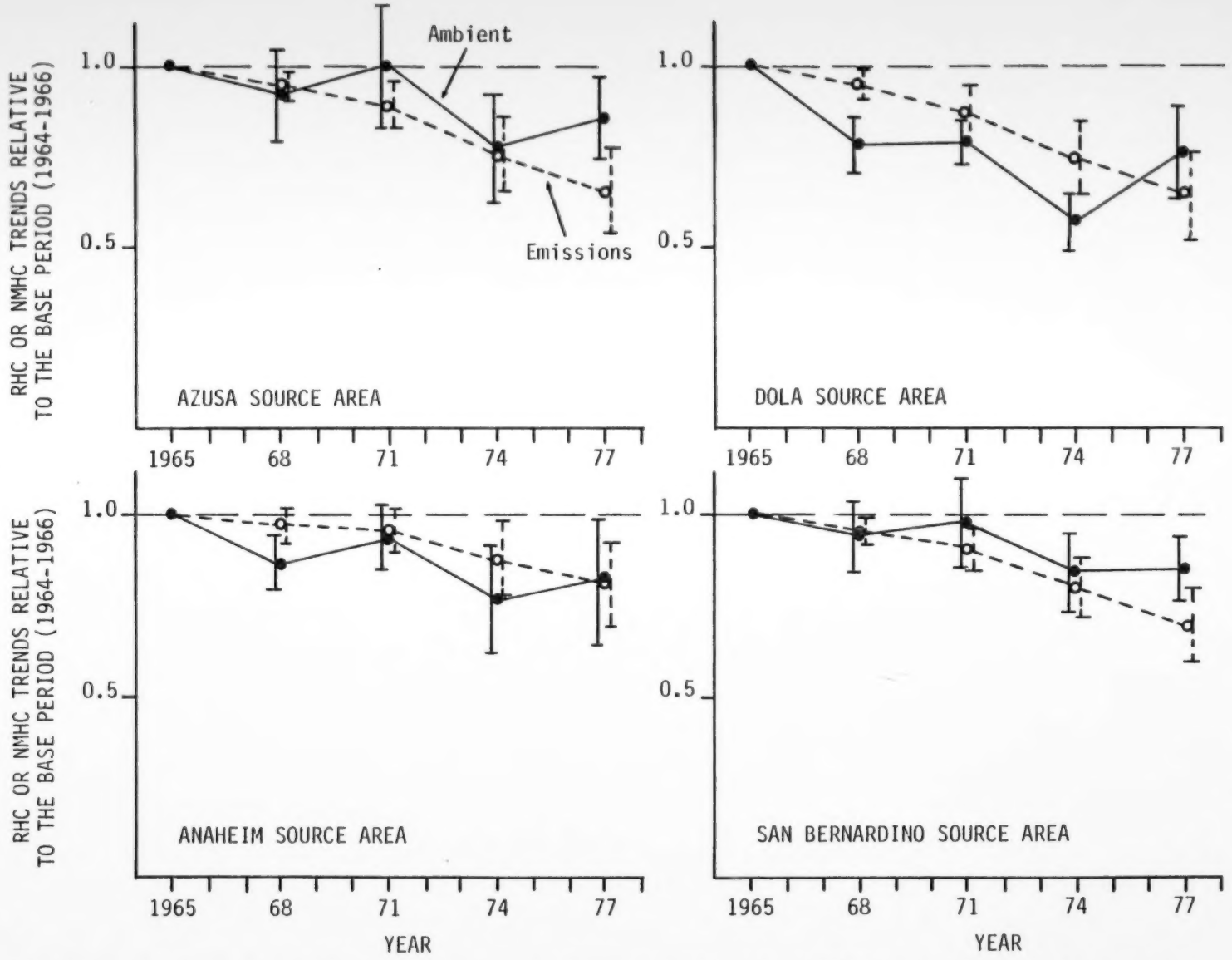

Figure 8. Comparison of RHC emission trends (o---o) with ambient NMHC trends (●——●) for various source areas in the Los Angeles region.

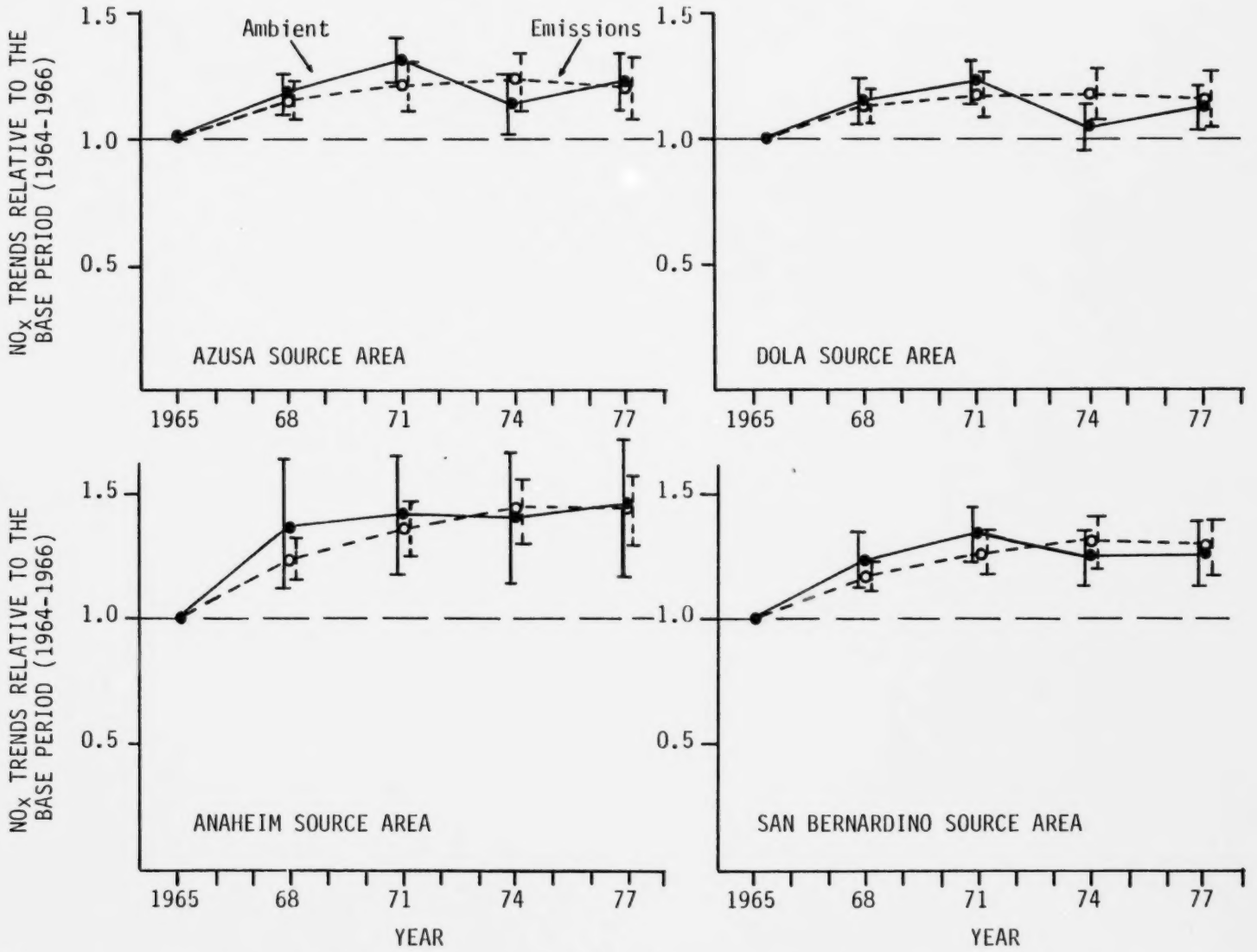

Figure 9. Comparison of NO_X emission trends (o---o) with ambient NO_X trends (●——●) for various source areas in the Los Angeles region.

source categories with individual growth/control levels that are sometimes hard to estimate with good precision.*

A final feature of Figures 8 and 9 that we will need to reference later (in Chapter 5), is the possibility of a meteorological anomaly during the 1970s. Specifically, it seems that the years 1973-1975 may have had significantly better dispersive conditions for the ozone precursors than the years 1970-1972 or 1976-1978. This possibility is suggested by the following observations. From 1970-1972 to 1973-1975, ambient NMHC declined at a faster rate than estimated RHC emissions, and ambient NO_x exhibited a moderate ($\sim$ 10-20%) decline despite a 5-10% increase in estimated NO_x emissions. From 1973-1975 to 1976-1978, ambient NMHC increased ($\sim$ 5-10%) despite a 10% decrease in estimated RHC emissions, and ambient NO_x increased ($\sim$ 5-10%) despite nearly constant NO_x emissions.

For future reference, it is also worthwhile at this time to make a brief comparison of predicted ozone trends based on emission changes with predicted ozone trends based on ambient precursor changes. For this comparison, we will use a base year ozone value corresponding to the 95th percentile of daily maximum ozone at each site and the EKMA test conditions selected later in Chapter 4 (base year NMHC/NO_x ratio of 13:1 and special EKMA isopleths with fixed-time irradiations, Los Angeles specific dilution rates, "characteristic curve" dilution pattern, and post 8 AM emissions).** Figure 10 shows that the predicted trends based on emission changes are fairly close to the predicted trends based on ambient precursor changes. In fact, we will show later (in Chapter 5), that when predicted ozone trends diverge from actual ozone trends, the divergence is approximately the same whether we use emission changes or ambient precursor changes in deriving predicted ozone trends.

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*It is especially difficult to compile growth/control schedules for the various categories of organic solvent use. Growth/control schedules for gasoline marketing, on the other hand, can be determined with good precision.

**The reader is referred to Chapter 4 for a detailed discussion of the chosen EKMA test conditions.

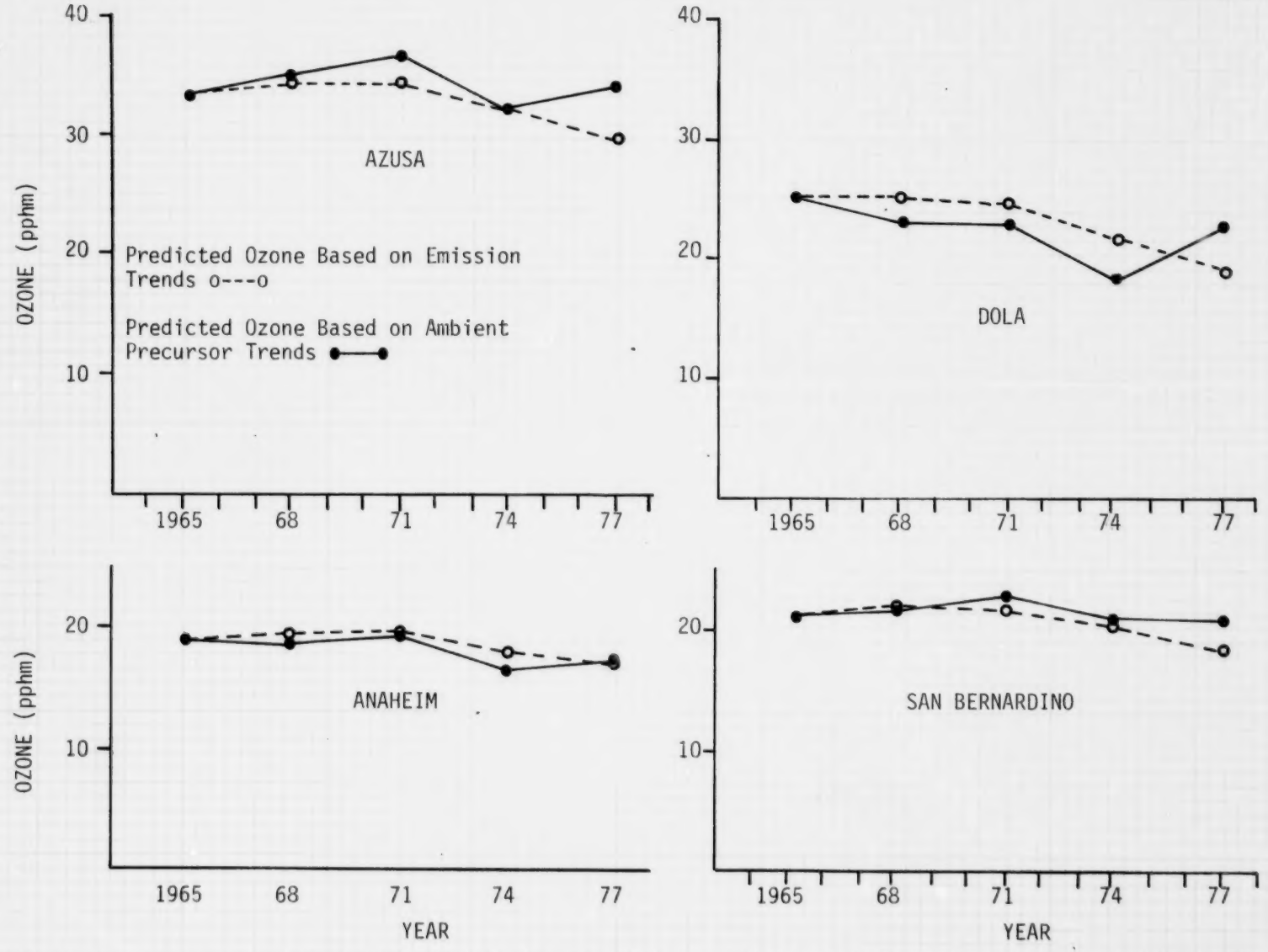

Figure 10. Comparison of predicted trends for the 95th percentile of daily maximum ozone using the EKMA method with emission changes and with ambient precursor changes.

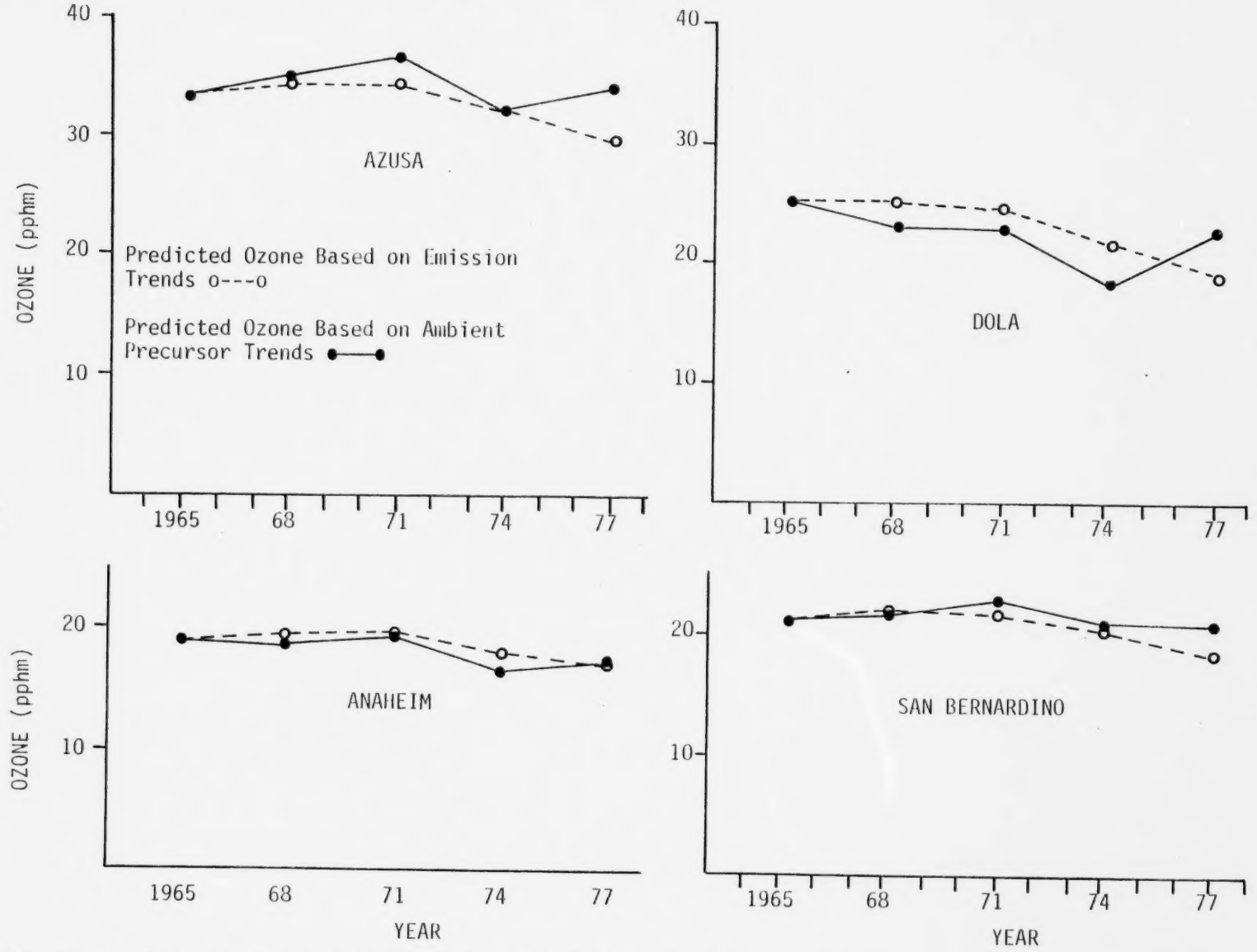

Figure 10. Comparison of predicted trends for the 95th percentile of daily maximum ozone using the EKMA method with emission changes and with ambient precursor changes.

CHAPTER 3

HISTORICAL OZONE TRENDS

Information on historical ozone trends in Los Angeles is another input required to check the EKMA isopleth method.* Basinwide trend data are needed to check the isopleths for the basinwide ozone maximum; trend data at individual locations are needed to check the isopleths for individual irradiation times. This chapter discusses the selection of monitoring sites and ozone trend indices, describes adjustments and corrections that have been applied to the ozone trend data, and tabulates the ozone trend data that will be used in the EKMA validation study.

SELECTION OF MONITORING SITES AND AIR QUALITY INDICES

Figure 11 illustrates the 13 monitoring stations in the Los Angeles basin that provide fairly complete ozone trend data over the 15-year study period, 1964-1978 (Trijonis 1980). When we refer to yearly basinwide maximum ozone, we mean the maximum ozone for a given year among these 13 stations. An alternative would be to define the yearly basinwide maximum as the maximum among any of the rather large number of stations that have been operated at various times during the study period. We decided against this alternative because it would bias the ozone trends due to the introduction of new stations (e.g. Upland) which better represented the high ozone areas of the basin in later years.

In addition to trends in basinwide maximum ozone, our study will consider trends in ozone at four individual locations: Downtown Los Angeles (DOLA), Anaheim, Azusa, and San Bernardino. The ozone trends at these sites will be used to check EKMA isopleths for individual irradiation times. These four locations typically experience maximum ozone concentrations around 1:00 PM, 1:30 PM, 2:00 PM, and 3:30 PM, respectively. Since the EKMA model uses

*As discussed in Chapter 1, we have decided to refer to the ambient trend data as "ozone" data despite the fact that nearly all the data actually consist of "oxidant" measurements made with the KI method.

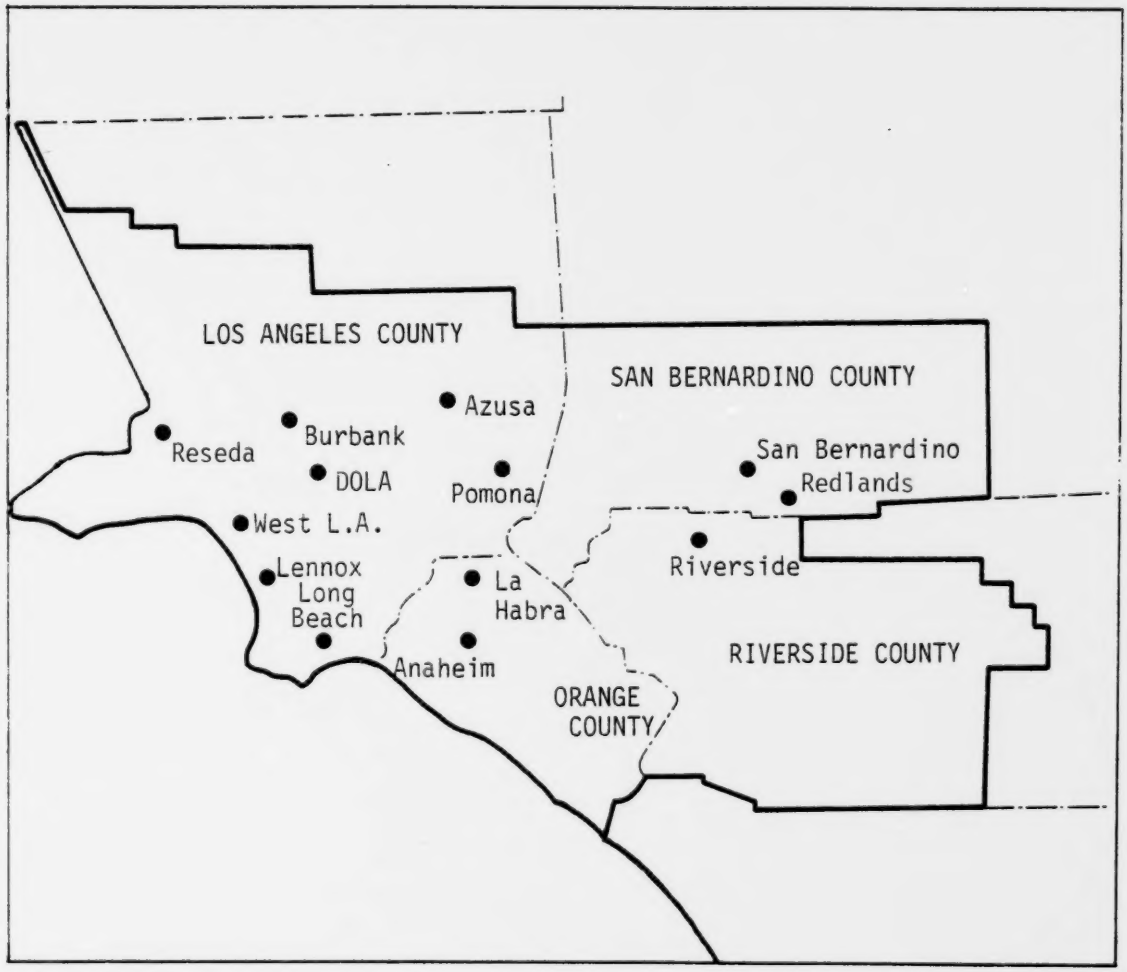

Figure 11. Thirteen monitoring stations in Los Angeles providing long-term historical trend data for ozone.

an 8 AM starting time, irradiation times of 5 hours, 5½ hours, 6 hours, and 7½ hours will be used for DOLA, Anaheim, Azusa, and San Bernardino, respectively.

In selecting ozone air quality indices for the validation studies, there are two important considerations. First, because the EKMA isopleth model applies to days of maximal ozone, the validation studies require air quality indices that are representative of high ozone days. Second, because the statistical variation in ambient ozone levels constitutes one of the critical error bounds in our analysis, we would like to select air quality indices that exhibit relatively low year-to-year variance. Table 8, based on 11 years of data at 11 Los Angeles locations, summarizes the overall magnitude and year-to-year variance of various ozone air quality indices. It is obvious that a trade-off exists between indices that are representative of high ozone days and those that have a low yearly standard deviation. The indices "yearly maximum concentration" and "yearly second maximum concentration" reflect worst-case days but display a yearly standard deviation of ± 17%. The indices "annual mean of all hours" and "yearly mean of daily maximum one-hour" have a variance of only ± 11% but do not adequately represent high ozone conditions.

For the validation studies, we have selected two ozone air quality indices: the yearly maximum concentration and the 95th percentile of daily maximum one-hour concentrations.* The yearly maximum concentration is of interest because it represents worst-case conditions. The 95th percentile of daily maximum one-hour concentrations is a good index for the validation studies because it reflects high ozone days but exhibits relatively low yearly variance. Both indices will be used for the validation tests at the

*It is somewhat of a toss-up in choosing between the yearly maximum concentration and the yearly second maximum concentration as a worst-case air quality index. We have selected the former because summary data are more readily available for that index. Also, it should be noted that we originally intended to include a third index -- the yearly mean of daily maximum one-hour concentrations. We found, however, that the ozone levels for this index were too low for effective use of the graphical EKMA technique.

TABLE 8. AVERAGE YEARLY VALUES AND YEAR-TO-YEAR DEVIATIONS FOR OZONE FOR VARIOUS AIR QUALITY INDICES IN LOS ANGELES (Trijonis and Hunsaker 1978).

OZONE AIR QUALITY INDEX	MEAN VALUE OF INDEX FOR 11 LOCATIONS DURING 1965-1975 (pphm)	DE-TRENDED YEAR-TO-YEAR DEVIATION AVERAGED OVER 11 LOCATIONS (as percent of mean value for the index)
1. Yearly Maximum 1-Hour	33.3	± 17.0%
2. Second Highest 1-Hour	30.8	± 16.5%
3. 99th Percentile of Daily Maximum 1-Hour	26.9	± 13.0%
4. 95th Percentile of Daily Maximum 1-Hour	20.3	± 11.5%
5. 99th Percentile of All Hours	17.4	± 11.5%
6. 90th Percentile of Daily Maximum 1-Hour	17.0	± 11.9%
7. 3rd Quarter Mean of Daily Maximum 1-Hour	13.2	± 14.2%
8. 95th Percentile of All Hours	10.9	± 12.1%
9. Yearly Mean of Daily Maximum 1-Hour	8.6	± 10.6%
10. Annual Mean of All Hours	3.0	± 11.1%

four individual monitoring sites; only the yearly maximum will be used for the basinwide analysis.

ADJUSTMENTS AND CORRECTIONS TO THE TREND DATA

It should be noted that the ozone trend data reported here have been subjected to several adjustments discussed by Trijonis (1980). The adjustments are as follows:

- All ozone data in Orange, Riverside, and San Bernardino Counties prior to June 1975 have been multiplied by a factor of 0.80 to account for a change in calibration procedures.
- Chemiluminescent and photometric ozone data have been multiplied by a factor of 0.90 to make them approximately equivalent to KI oxidant data. This factor accounts for the oxidant to ozone monitoring switch in Riverside and San Bernardino Counties during the early 1970s.
- Data for certain station-years have been filled in by interpolation or extrapolation. For the four individual monitoring sites considered here, the only such fill-ins are as follows: Anaheim 1975 (incomplete year of data), Anaheim 1978 (KI oxidant measurements discountinued), and San Bernardino 1972 [erroneous data noted by Zeldin (1978)].

Duckworth et al. (1980) and Kinosian (1980) have reported the possibility of a major "glitch" in the ozone trend data for Los Angeles County. Specifically, they indicate that there may have been an artificial downward jump in ozone during 1970-1972. As described in Appendix B, we have scrutinized ozone trend data at ten locations in two counties in order to investigate this possible aberration. We have concluded that there probably is no significant artificial jump in the data. There certainly is no consistent aberration occurring at all Los Angeles County sites. There could be a problem at Azusa and Pomona, but we find it hard to imagine why the error would occur only at those two sites. It seems more reasonable that those two

proximate sites both measured an unusual (but real) ozone drop in eastern Los Angeles County from 1970 to 1972.

OZONE TREND DATA AND ERROR BARS

Table 9 presents the ozone trend data to be used in the EKMA validation tests. The table lists 3-year averages for various ozone air quality indices, beginning with the base period 1964-1966 and continuing through 1976-1978. The air quality indices are the basinwide yearly maximum, the yearly maximum at the four study sites, and the 95th percentile of daily maxima at the four study sites. The trend data are also illustrated in Figures 12 to 16; these figures present the yearly data as well as the 3-year averages.

Figures 12 to 14 show that ozone concentrations decreased at Azusa, DOLA, and Anaheim from the middle 1960s to the early/middle 1970s and then leveled off. All sites in Los Angeles except for those in the extreme eastern part of the basin exhibit this qualitative pattern in ozone trends (Trijonis 1980). Figure 15 shows that ozone at San Bernardino increased at a very slight rate during the entire study period. This reflects the general ozone trend at sites in the extreme eastern parts of the basin (Trijonis 1980).

For the purposes of the EKMA validation study, the error bounds on the actual ozone trends should represent the meteorological variance in those trends. As indicated previously in Table 8, the typical year-to-year variance is ± 17% for the yearly maximum ozone concentration and ± 11.5% for the 95th percentile of daily maximum ozone. Because we are dealing with 3-year averages, these error values should be divided by the square root of 3. Because we are examining differences relative to a base period (1964-1966), the error values should be multiplied by the square root of 2. Accordingly, the meteorological error in the actual ozone trends is 17.0% x $\sqrt{2/3}$ or 13.9% for the yearly maximum and 11.5% x $\sqrt{2/3}$ or 9.4% for the 95th percentile of daily maxima. Examining the overall ozone levels for the study sites as listed in Table 9, we see that the meteorological errors in the actual ozone trends are approximately as listed in Table 10.

TABLE 9. AMBIENT OZONE TRENDS FOR THE EKMA VALIDATION STUDY (IN PPHM).

3-YEAR PERIODS	3-YEAR AVERAGES OF 95TH PERCENTILE OF DAILY MAXIMUM 1-HOUR OZONE				3-YEAR AVERAGES OF YEARLY 1-HOUR MAXIMUM OZONE				
	Azusa	DOLA	Anaheim	San Bernardino	Azusa	DOLA	Anaheim	San Bernardino	Basinwide
1964-66	33.3	25.3	18.9	21.1	49.0	51.3	31.5	31.2	52.3
1967-69	35.0	22.3	17.1	20.3	54.3	37.3	29.3	29.1	56.0
1970-72	32.0	18.0	13.1	22.8	51.7	27.3	30.1	30.2	51.7
1973-75	27.0	18.0	13.2	22.7	38.8	34.0	25.7	32.0	46.6
1976-78	27.1	17.7	13.3	23.2	36.7	28.3	26.7	30.6	41.3

TABLE 10. METEOROLOGICAL ERROR IN ACTUAL OZONE TRENDS USED IN THE EKMA VALIDATION STUDY.

SITE	ERROR FOR YEARLY MAXIMUM OZONE	ERROR FOR 95TH PERCENTILE OF DAILY MAXIMA OZONE
Basinwide	7 pphm	—
Azusa	6½ pphm	3 pphm
DOLA	5 pphm	2 pphm
Anaheim	4 pphm	1½ pphm
San Bernardino	4½ pphm	2 pphm

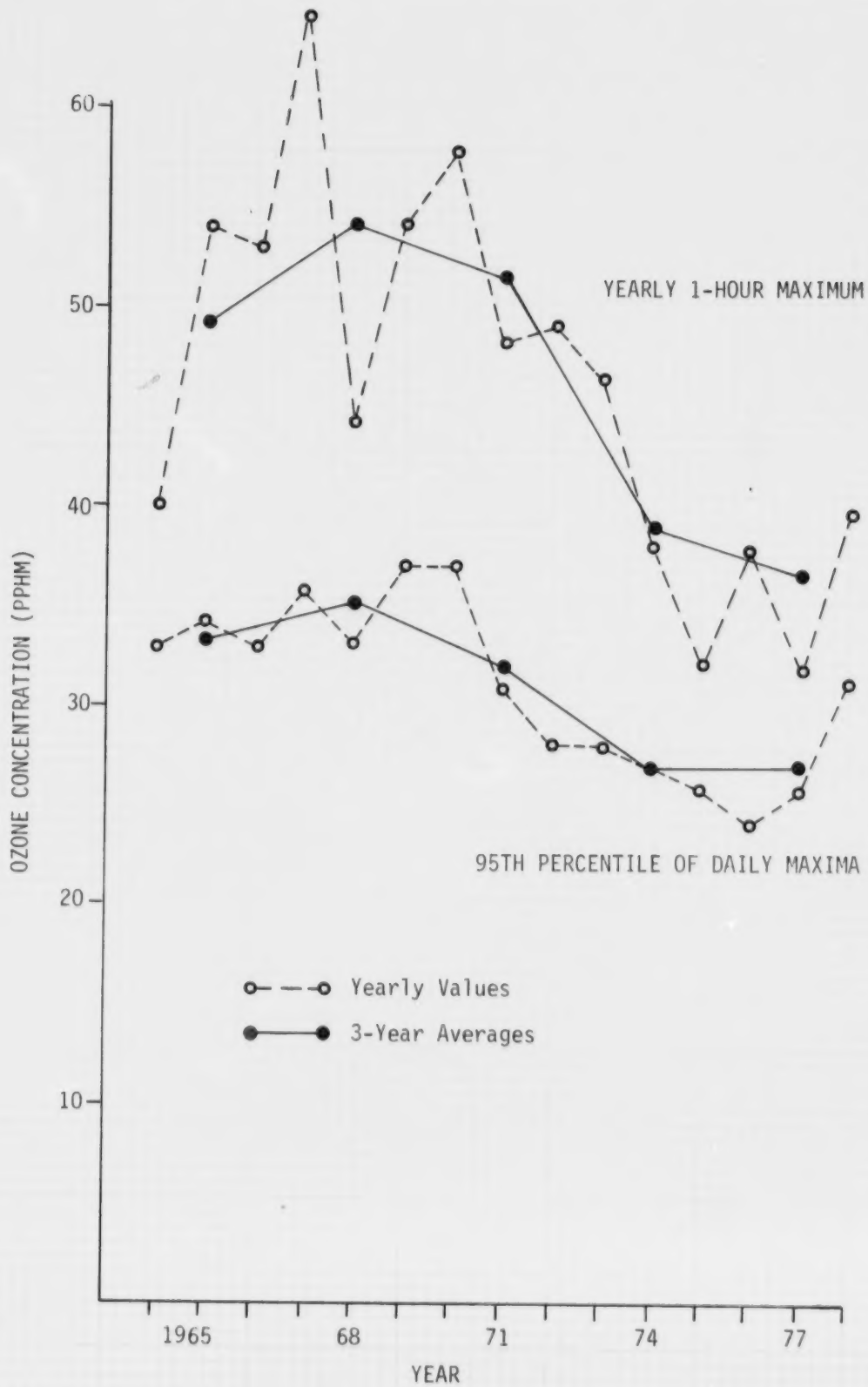

Figure 12. Historical ozone trends at Azusa.

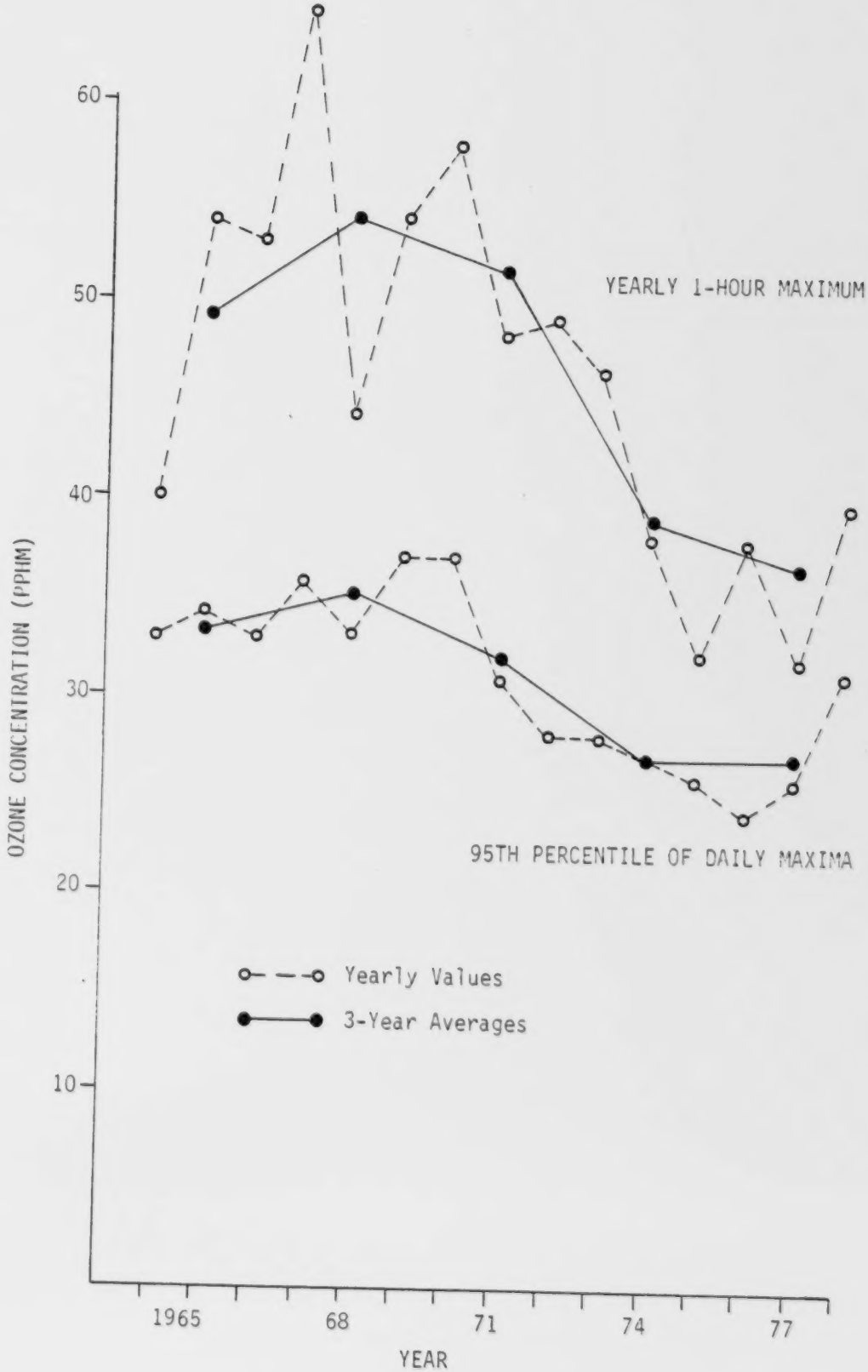

Figure 12. Historical ozone trends at Azusa.

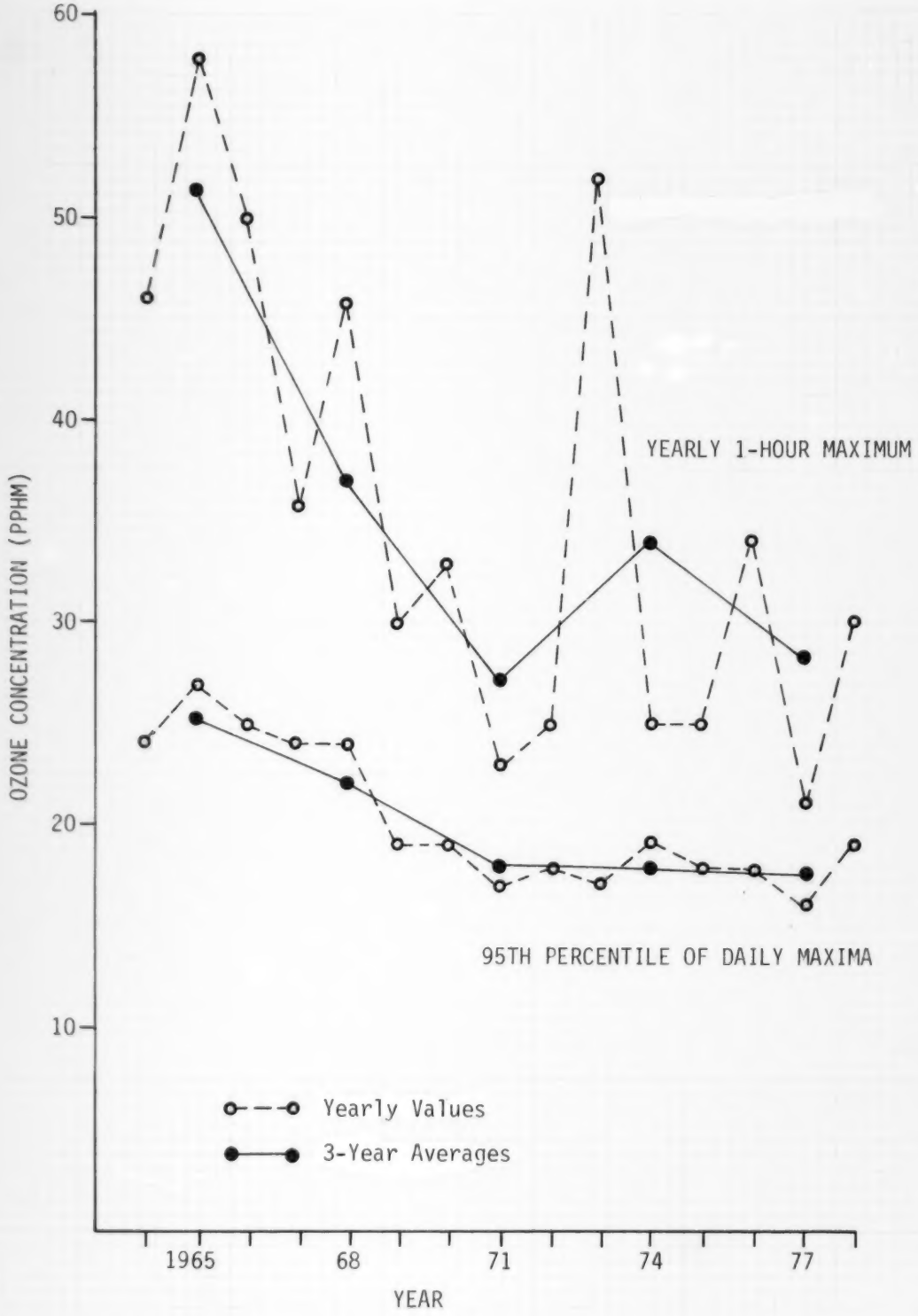

Figure 13. Historical ozone trends at DOLA.

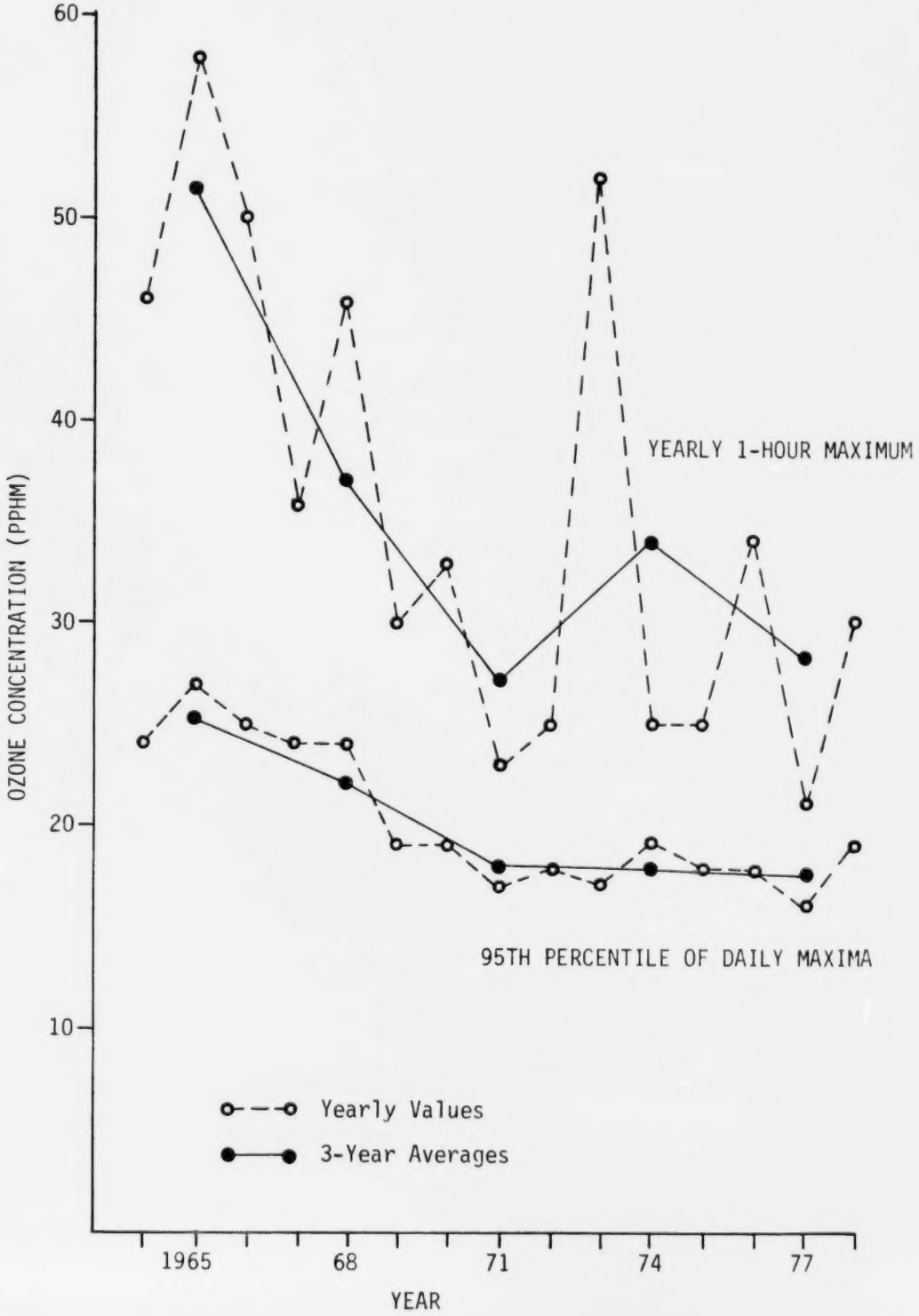

Figure 13. Historical ozone trends at DOLA.

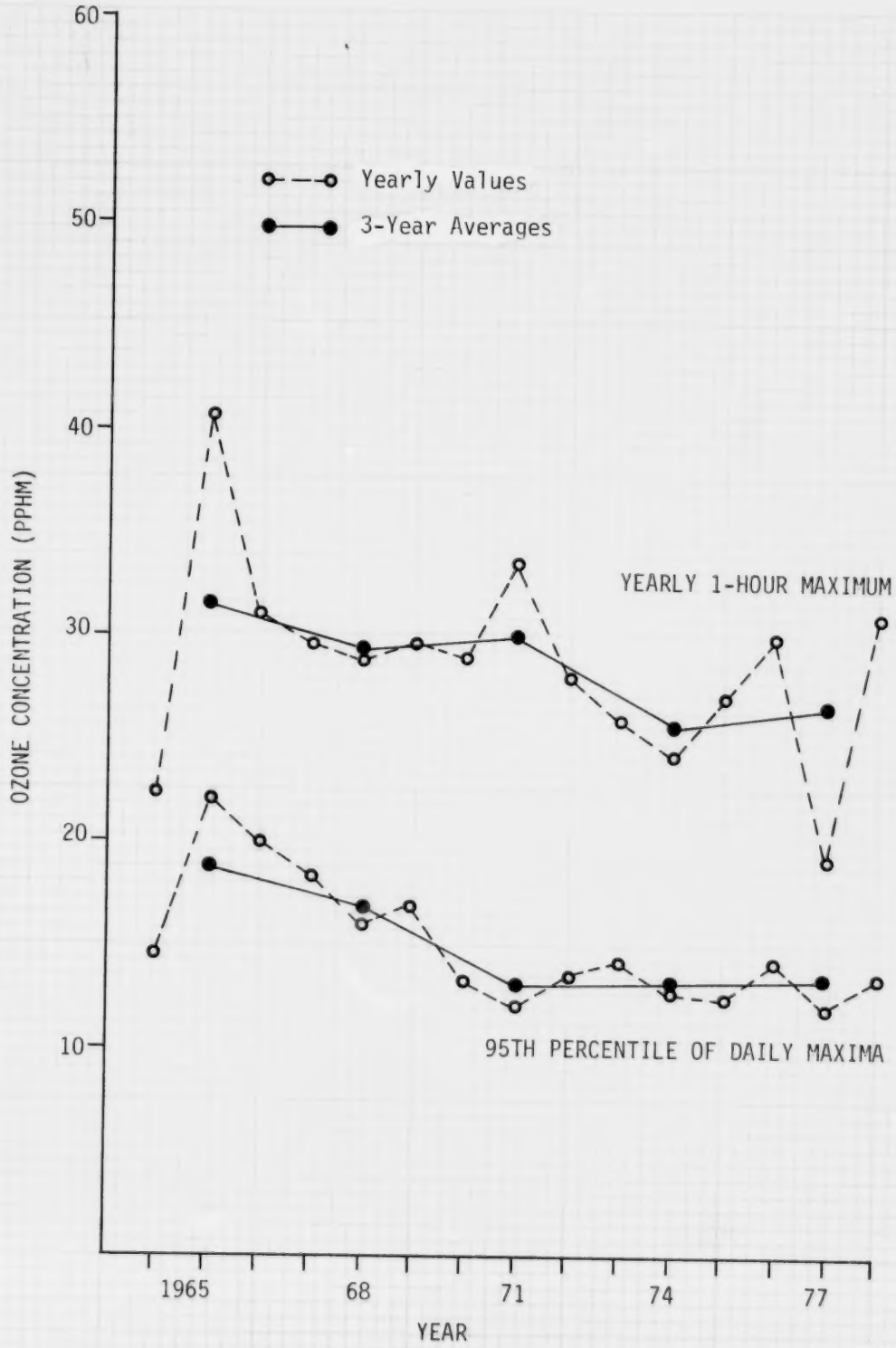

Figure 14. Historical ozone trends at Anaheim.

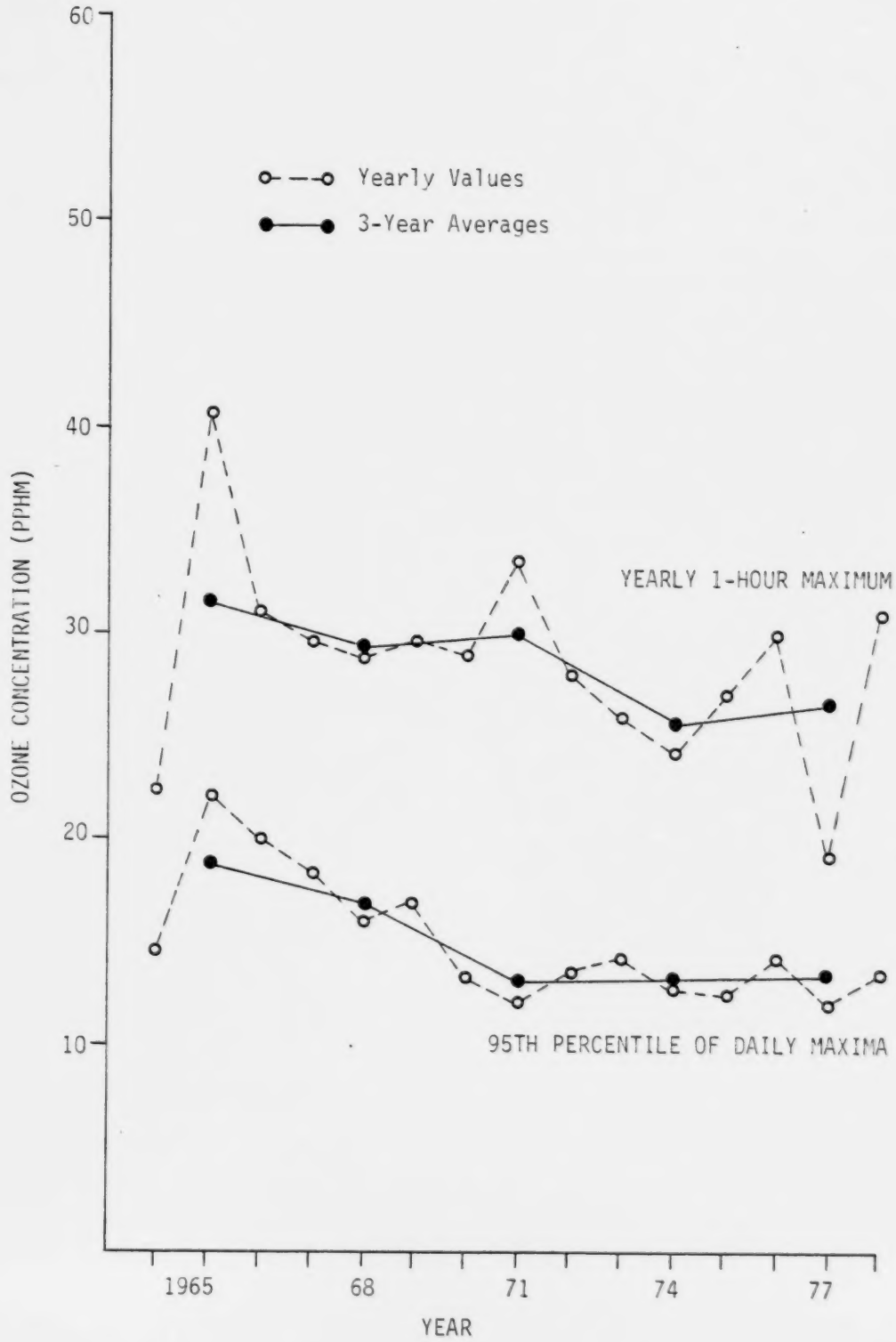

Figure 14. Historical ozone trends at Anaheim.

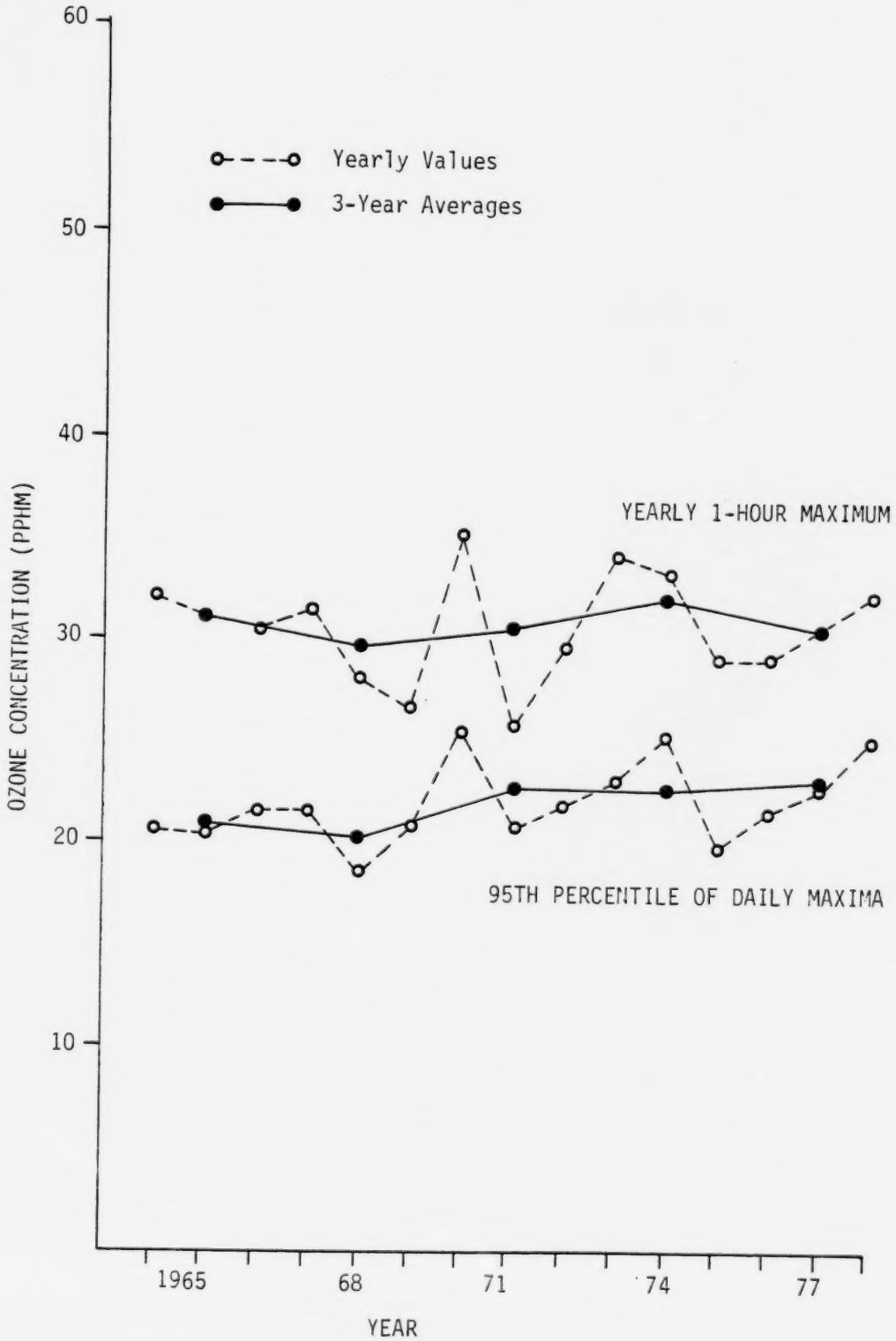

Figure 15. Historical ozone trends at San Bernardino.

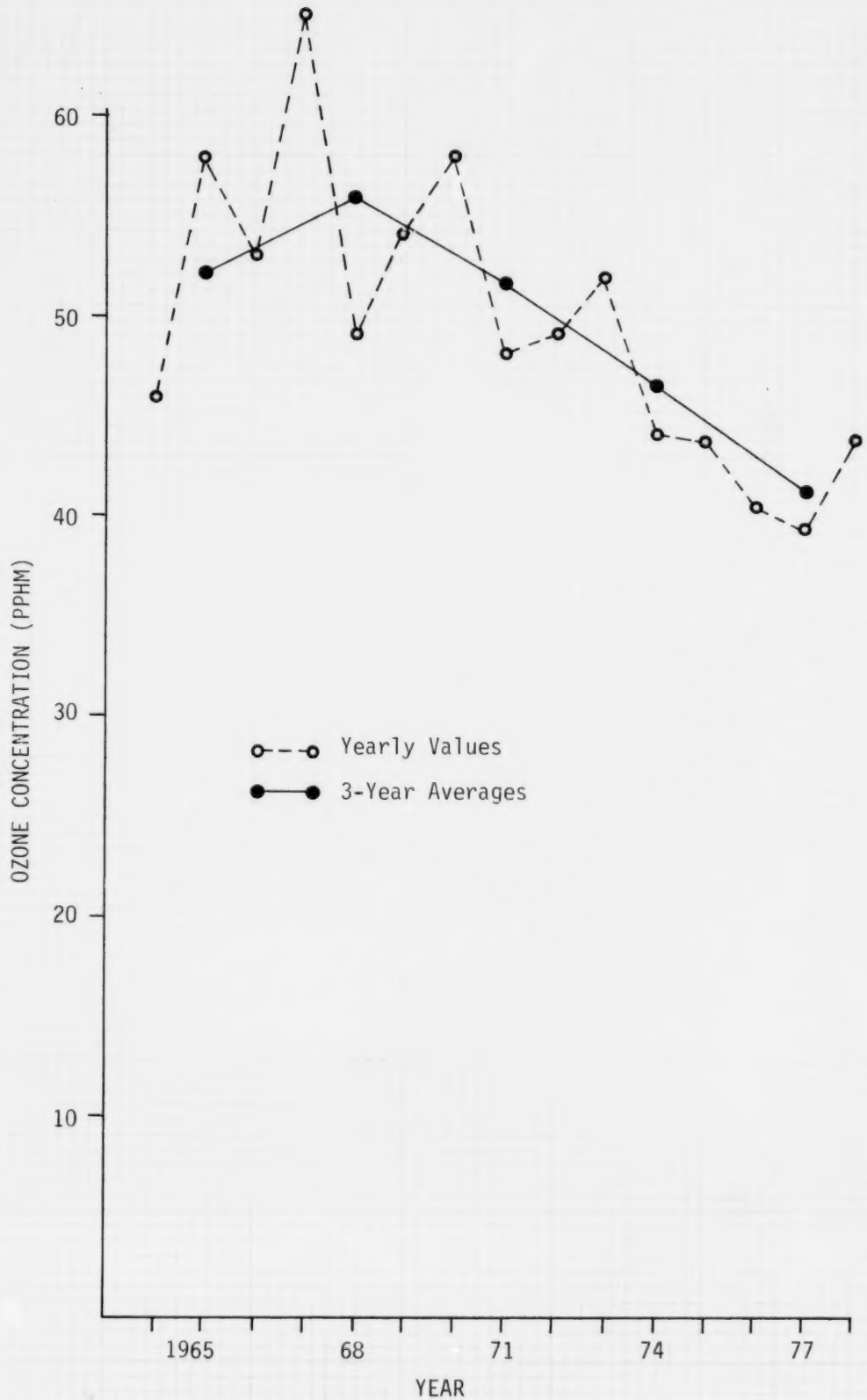

Figure 16. Historical trends for basinwide maximum ozone in the Los Angeles region.

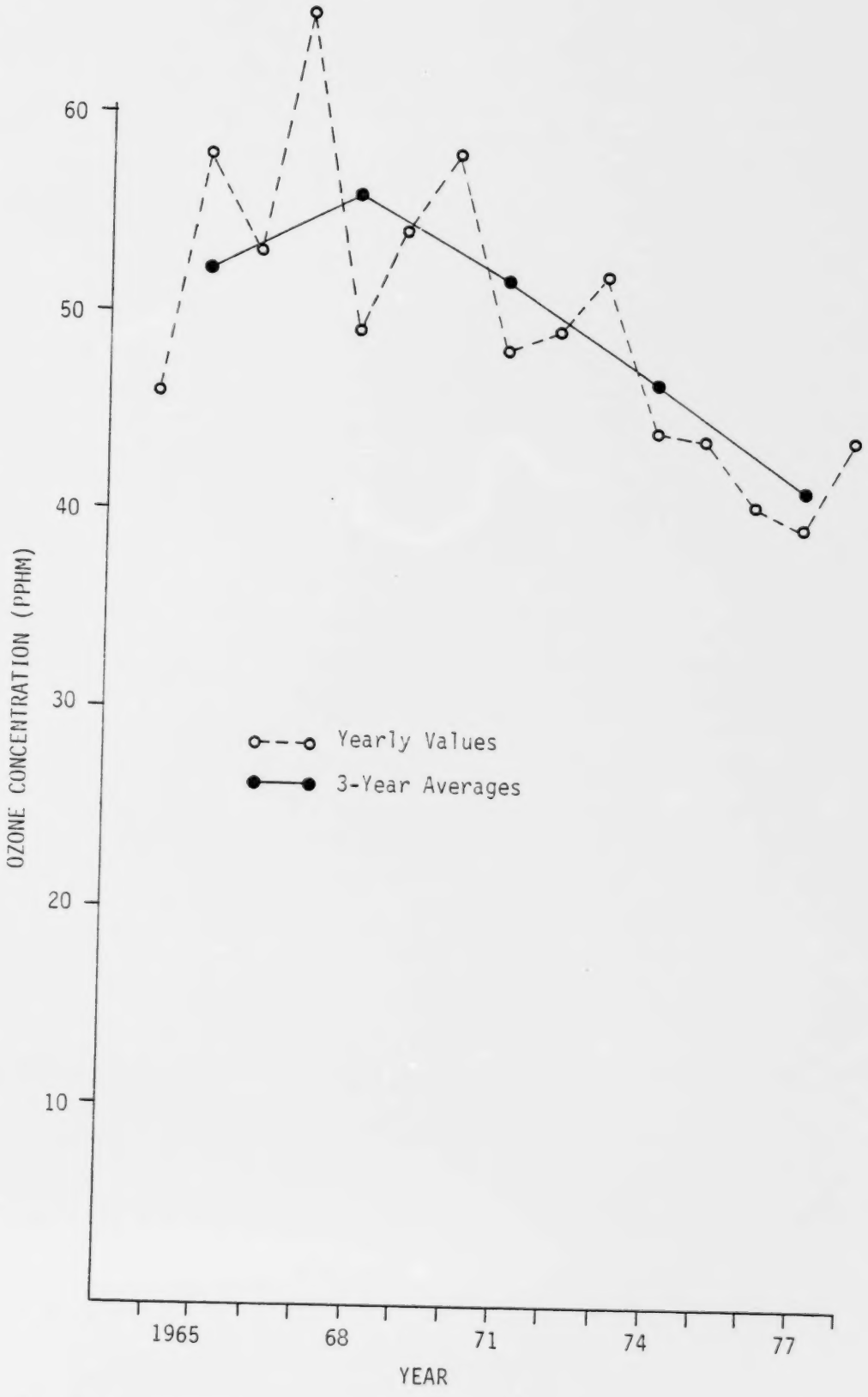

Figure 16. Historical trends for basinwide maximum ozone in the Los Angeles region.

CHAPTER 4

SELECTION OF SPECIFIC CONDITIONS FOR EKMA VALIDATION

Before proceeding with validation of the EKMA model, two more preliminary issues must be resolved. One is the choice of NMHC/NO_x ratios to be used with the isopleth method; the other is the selection of specific EKMA simulation conditions. This chapter provides a thorough discussion of data for the NMHC/NO_x ratio in Los Angeles and presents a sensitivity analysis using EKMA isopleths generated under various simulation conditions.

NMHC/NO_x RATIO

In predicting ozone trends with the EKMA model, one of the critical inputs is the ambient 6-9 AM NMHC/NO_x ratio for the base period (1964-1966). In order to estimate the 1964-1966 NMHC/NO_x ratio, we start by examining data on the ambient ratio for the early to middle 1970s. The early to middle 1970s is the period for which there is the most abundant data on the ratio from various monitoring programs.

Table 11 summarizes ambient data on the median 6-9 AM NMHC/NO_x ratio.* Estimates of the median NMHC/NO_x ratio are provided both for randomly selected summer days and for summer days of highest ozone (the latter are distinguished by parentheses in the table). As discussed in the footnotes to the table, certain corrections have been applied to the data. For example, the NMHC data have been adjusted to be equivalent to measurements made with propane calibrated instruments [this is to make the NMHC measurement techniques equivalent to the technique used in the chamber studies that serve as a foundation for EKMA (Dimitriades 1970, 1972, 1977b)].

At first glance, the variation in the median 6-9 AM NMHC/NO_x ratio shown in Table 11 is disturbingly large. However, closer scrutiny of the

*Note that routine NMHC data taken by the Southern California AQMD in Los Angeles County are excluded from this table because of known problems with this data that cause serious underestimates of NMHC concentrations (Eldon and Trijonis 1977).

TABLE 11. MEASUREMENTS OF THE MEDIAN 6-9 AM AMBIENT NMHC/NO_x RATIO FOR THE LOS ANGELES BASIN IN THE EARLY/MIDDLE 1970s.

DATA SOURCE	CORRECTIONS APPLIED (See Footnotes)	MONITORING LOCATIONS	TIME PERIOD	MEDIAN RATIO OF NMHC/NO_x	MEDIAN RATIO ÷ 10TH PERCENTILE RATIO	90TH PERCENTILE RATIO ÷ MEDIAN RATIO
Routine ARB monitoring data for NMHC and NO_x	a	Temple City	19 summer days, 1976	11	2.0	1.3
			9 high O_3 summer days, 1976	(14)	(NC)	(NC)
		DOLA	5 high O_3 summer days, 1976	(8)	(NC)	(NC)
Routine monitoring data for NMHC and NO_x by the Statewide Air Pollution Research Center	a	Riverside	9 summer days, 1976	11	1.3	2.5
Special field study data, the Los Angeles Reactive Pollutant Program	b	Central Los Angeles Area	13 summer days, 1973	5	1.7	2.0
Routine AQMD monitoring data for THC and NO_x. The THC data are converted to NMHC using an empirical formula developed by the ARB based on El Monte Laboratory NMHC data.	c	DOLA	All summer days, 1971-1975	10	1.7	1.7
			50 highest O_3 summer days, 1971-1975	(11)	(1.7)	(1.4)
ARB El Monte Laboratory NMHC data with routine AQMD NO_x data.		Azusa	30 summer days, 1971	8	1.1	1.6
			30 summer days, 1974	21	1.4	1.4
		DOLA	30 summer days, 1971	8	2.0	1.4
			30 summer days, 1974	15	1.4	1.9
			5 high O_3 summer days, 1976	(9)	(NC)	(NC)

a The NMHC data are divided by 0.7 to make methane calibrated instruments approximately equivalent to propane calibration (Horie et al. 1979). The 0.7 factor is a crude first-order correction factor; the actual differences between methane and propane calibration depend on the specific hydrocarbon mix as well as the specific monitoring device.

b The NMHC data are multiplied by 0.75 to account for special LARPP calibration procedures.

c The empirical formula relating THC to NMHC is NMHC = 0.7(THC - 1.5), with units of ppmC (Paskind and Kinosian 1974).

NC Not calculated.

Note: Values in parentheses are for high ozone days.

table reveals that most of the data sets indicate a median ratio of 8:1 to 11:1. The three exceptions are the LARPP data for central Los Angeles (a median of 5:1), the routine ARB Temple City data on high ozone days (a median of 14:1), and the 1974 El Monte Laboratory data at DOLA and Azusa (medians of 15:1 and 21:1). We are not sure why these three data sets give anomalous values. One possible explanation is the small number of days included in the samples. Also, the LARPP data are based on a very unusual calibration procedure (THC calibrated with propane and methane calibrated with methane). Furthermore, we previously have questioned the accuracy of the 1974 El Monte Laboratory data (Trijonis and Hunsaker 1978).

Table 11 does not reveal any obvious spatial gradients in the ratio (e.g. the western Los Angeles basin versus the eastern Los Angeles basin) or any obvious trends in the ratio during the time period 1971 to 1976. The table does, however, suggest that, for equivalent data sets, the ratio is slightly higher on ozone episode days than on all summer days. A best guess of the ambient 6-9 AM ratio during the early to middle 1970s appears to be the range 8:1 to 11:1, with the higher part of this range more appropriate for high ozone days. Because the EKMA validation study is most concerned with days of highest ozone, we will take a value of 11:1 as the best guess for the ambient NMHC/NO_x ratio during the early/middle 1970s.

Two further adjustments must be made before we can select the median NMHC/NO_x ratio for our EKMA validation study. First, we note that the smog chamber studies on which EKMA is based contained very little (approximately 1%) of the nearly nonreactive NMHC compounds ethane and propane (Dimitriades 1980). Los Angeles atmospheric NMHC, on the other hand, contains about 10% ethane and propane (see Appendix C for a detailed discussion of ethane and propane fractions in Los Angeles NMHC). To account for this obvious reactivity difference, the ambient NMHC/NO_x ratio for Los Angeles in the early/middle 1970s should be adjusted downward by about 10%, from 11:1 to 10:1. Second, we need to convert the ratio for the early/middle 1970s to a ratio for 1964-1966. As shown in Figure 17, historical trend data indicate the

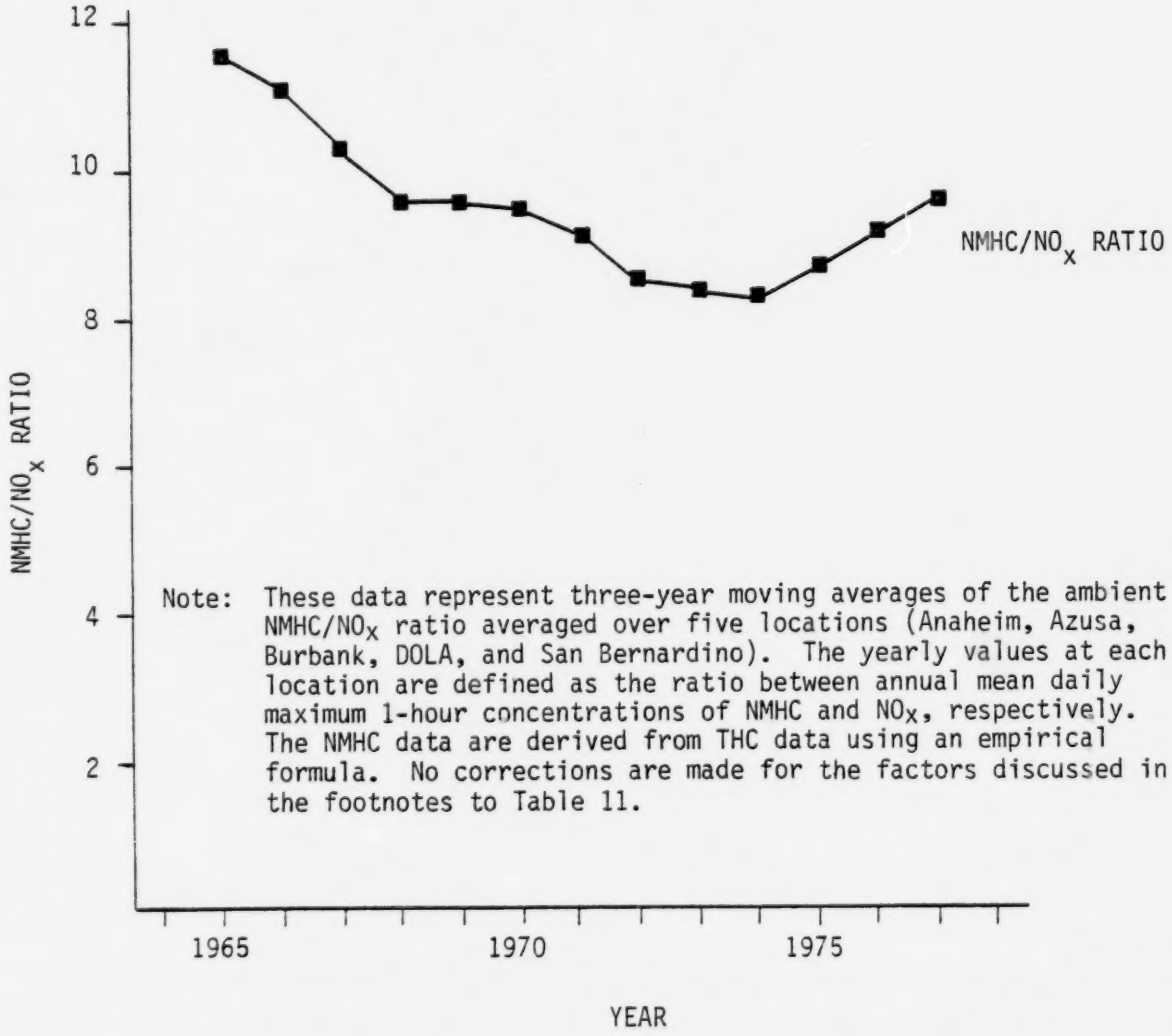
12
10
8
6
4
2
NMHC/NOx RATIO
NMHC/NOx RATIO
1965
1970
1975
YEAR
Note: These data represent three-year moving averages of the ambient NMHC/NOx ratio averaged over five locations (Anaheim, Azusa, Burbank, DOLA, and San Bernardino). The yearly values at each location are defined as the ratio between annual mean daily maximum 1-hour concentrations of NMHC and NOx, respectively. The NMHC data are derived from THC data using an empirical formula. No corrections are made for the factors discussed in the footnotes to Table 11.

Figure 17. Historical trends of the ambient $NMHC/NO_X$ ratio in the Los Angeles basin (Trijonis 1980).

ambient NMHC/NO_x ratio decreased by a factor of approximately 1.3 from the middle 1960s to the early/middle 1970s. This is qualitatively consistent with historical emission changes for hydrocarbons and NO_x.* Thus, our best estimate of the EKMA-equivalent 6-9 AM ratio in Los Angeles for high ozone days during the base period 1964-1966 is approximately 13:1.

Table 11 also demonstrates the statistical variance in the daily 6-9 AM ratio at given monitoring sites by indicating the relative magnitudes of the 10th percentile ratio and the 90th percentile ratio as compared to the median ratio. It is evident that the 10th and 90th percentile ratios each differ from the median ratio by a significant factor, on the order of 1.3 to 2.0.** Because of the stochastic day-to-day fluctuations in the ratio, and because of the uncertainties in the median ratio as exemplified by various monitoring programs, it is important to use a range of ratios in the EKMA validation study (i.e. to investigate the sensitivity of our results to changes in the base year NMHC/NO_x ratio). For the purpose of this sensitivity analysis, we have selected "low" and "high" ratios nearly a factor of 2.0 different from our median ratio. Specifically, the range we have chosen for the base period (1964-1966) NMHC/NO_x ratio is as follows:

BEST ESTIMATE:	13:1
LOW ESTIMATE:	7:1
HIGH ESTIMATE:	25:1

EKMA SIMULATION CONDITIONS

Isopleths of ozone versus initial NMHC and NO_x can be generated by the EKMA model under a variety of simulation conditions. The standard EKMA

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*Actually, our historical emission trend data for the entire basin (Chapter 2) indicate that the NMHC/NO_x emission ratio decreased by a factor of 1.6 from the middle 1960s to the early/middle 1970s.

**This is a multiplication factor for the 90th percentile ratio, and a division factor for the 10th percentile ratio.

isopleths (denoted by STANDARD in subsequent graphs) represent the following conditions:

- A 10 hour irradiation with diurnal sunlight intensity corresponding to 8 AM-6 PM LDT for the summer solstice at 34°N latitude (the latitude of Los Angeles).
- A dilution rate of 3% per hour for the first 7 hours and zero dilution thereafter (corresponding to a mixing height change from 510 meters at 8 AM to 630 meters at 3 PM).
- No emissions after 8 AM.
- No transported or advected ozone.
- A hydrocarbon mix of 25% propylene and 75% n-butane with aldehydes of 5% the initial NMHC.
- An initial NO_2/NO_x ratio of 0.25.
- Ozone value defined as maximum ozone during the 10 hour irradiation.

Herein we will consider not only the standard EKMA simulation conditions but also several refinements of those conditions. The first refinement is to use isopleths which represent ozone values at fixed irradiation times rather than maximum ozone values over the entire irradiation period. Such isopleths (denoted by FIXTIME in subsequent figures) would better simulate trends at fixed monitoring stations. As discussed in Chapter 3, the site-specific simulation times are 5 hours at DOLA, 5½ hours at Anaheim, 6 hours at Azusa, and 7½ hours at San Bernardino. The standard EKMA ozone value (maximum during ten hour irradiation) will, of course, be used when we consider trends in basinwide maximum ozone rather than trends at individual monitoring sites.

The second refinement is to use dilution rates characteristic of highest ozone days in Los Angeles (Meyer 1980). Specifically, we use isopleths (denoted by FIXTIME-LADILUTION) that assume a dilution rate of 17% per hour for the first nine hours with zero dilution thereafter. This dilution rate corresponds to a mixing height change from 150 meters at 8 AM to 600 meters

at 5 PM. As a further elaboration, we then add post 8 AM emissions to this type of model (using emission data specific to the Los Angeles region); this leads to isopleths that we denote as FIXTIME-LADILUTION-EMISSIONS.

The next refinement also assumes a mixing height change from 150 meters at 8 AM to 600 meters at 5 PM but uses a concave-downward "characteristic curve" to represent the diurnal mixing height variation (Schere and Demerjian 1978) rather than the convex exponential curve based on the 17% per hour dilution pattern. Such EKMA isopleths generated without post 8 AM emissions are denoted as FIXTIME-CHARCURVEDILUTION; those including post 8 AM emissions are referred to as FIXTIME-CHARCURVEDILUTION-EMISSIONS. A priori, we think that this last set of simulation conditions (fixtime irradiation, characteristic curve dilution, and post 8 AM emissions) should be the most appropriate set for the validation test. We will use this set in the final tests at the individual monitoring sites. For basinwide maximum ozone, we will use isopleths for maximum ozone during a ten-hour irradiation but including characteristic curve dilution and post 8 AM emissions.

One further major refinement of the EKMA simulation conditions might make sense. This refinement would be to include transported or advected ozone left over from previous days in the EKMA simulation. We did not include the advected ozone effect because a recent report (SCE 1980) suggests that previous day ozone layers which occur aloft in the Los Angeles basin do not interact significantly with present day pollution within the mixing layer. This issue deserves further investigation, however, and more validation tests might be conducted in the future with EKMA isopleths that do include advected ozone.

Sensitivity Analyses for the 13:1 NMHC/NO_x Ratio at the Four Study Sites

As a first step in conducting sensitivity analyses using the various EKMA isopleths, we consider predicted ozone trends for six types of isopleths at each of the four study sites using our best estimate for the median NMHC/NO_x ratio (13:1). Figures 18 through 21 present the results of the sensitivity analysis for the specific case of 95th percentile of daily maximum ozone, with predicted ozone trends based on ambient precursor

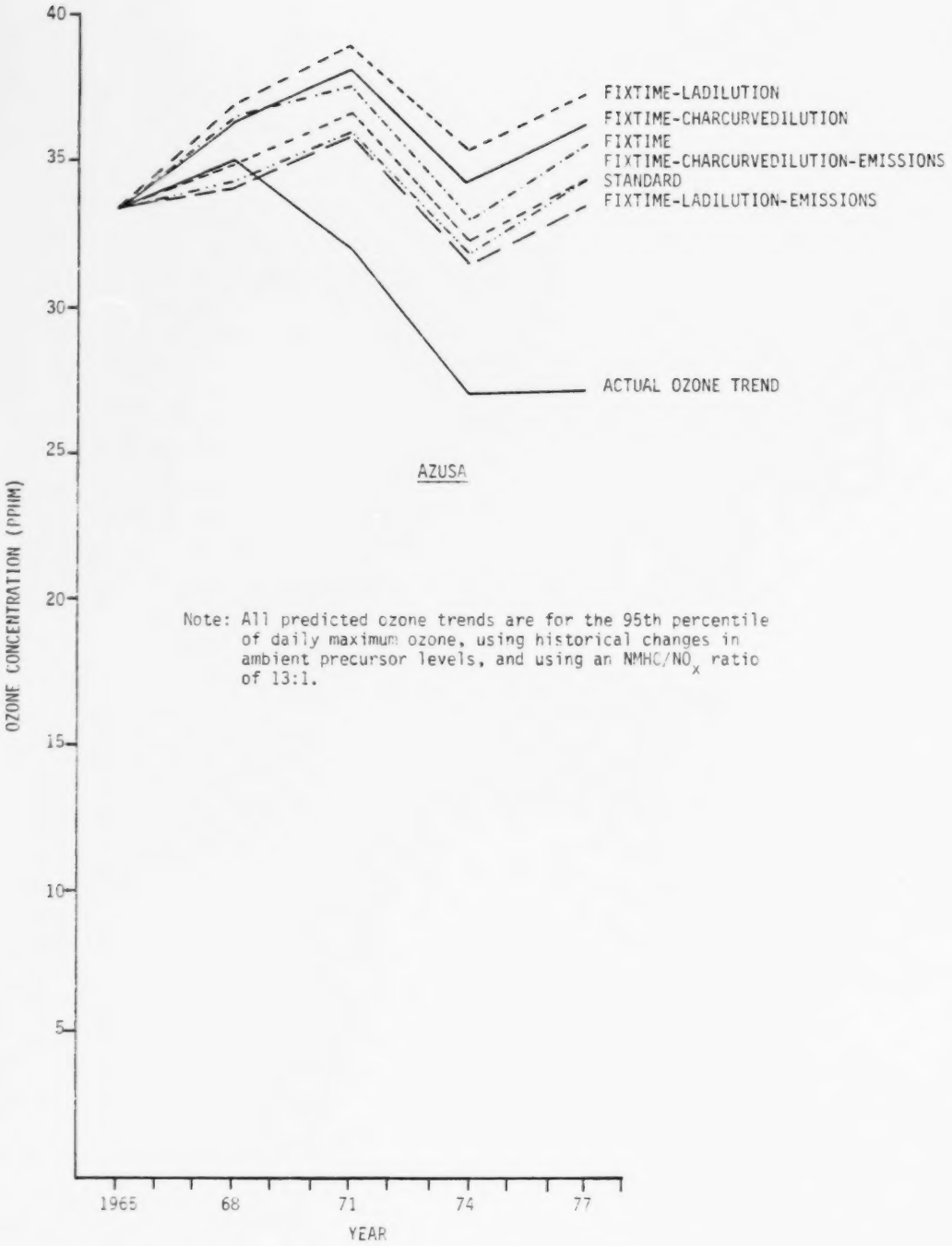

Figure 18. Sensitivity of predicted ozone trends at Azusa to various EKMA simulation conditions.

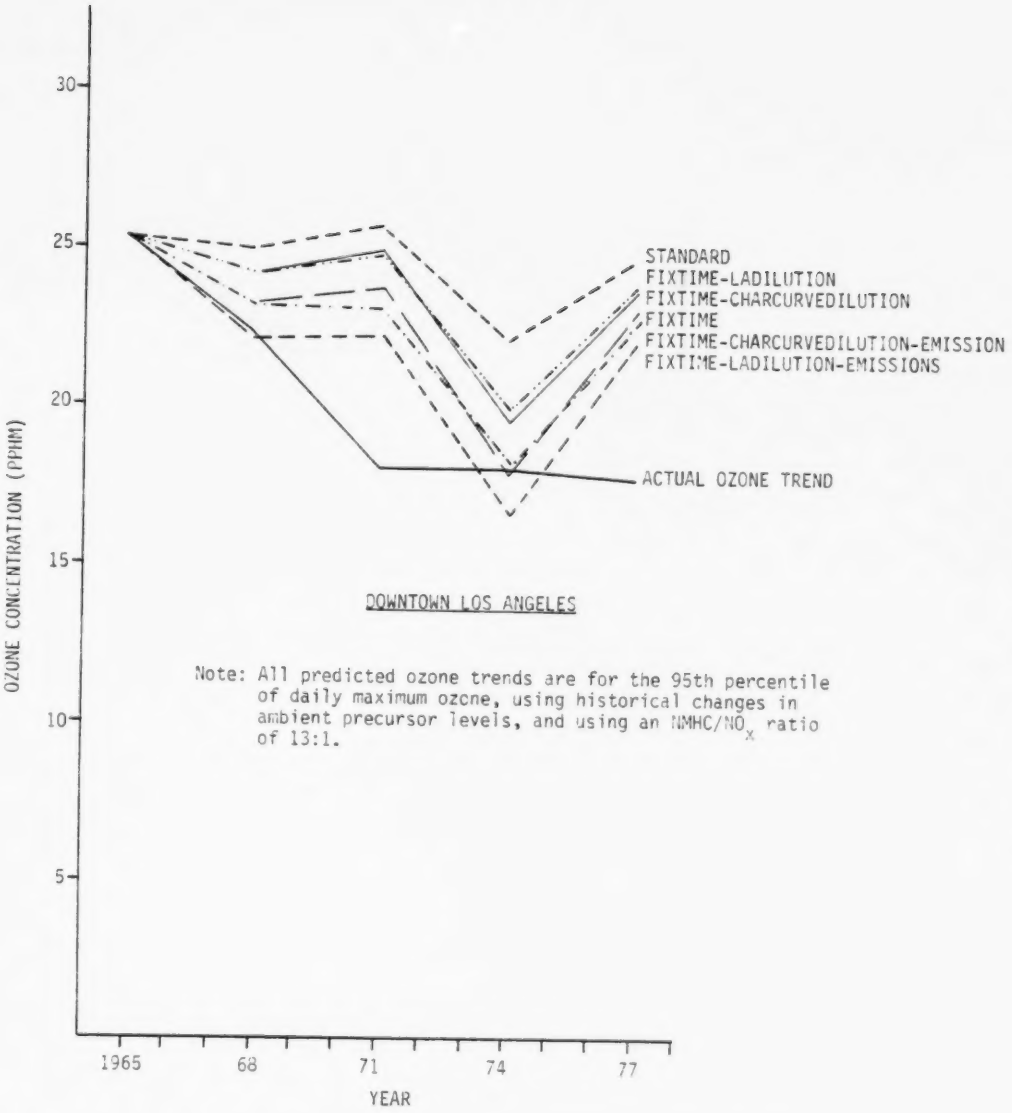

Figure 19. Sensitivity of predicted ozone trends at DOLA to various EKMA simulation conditions.

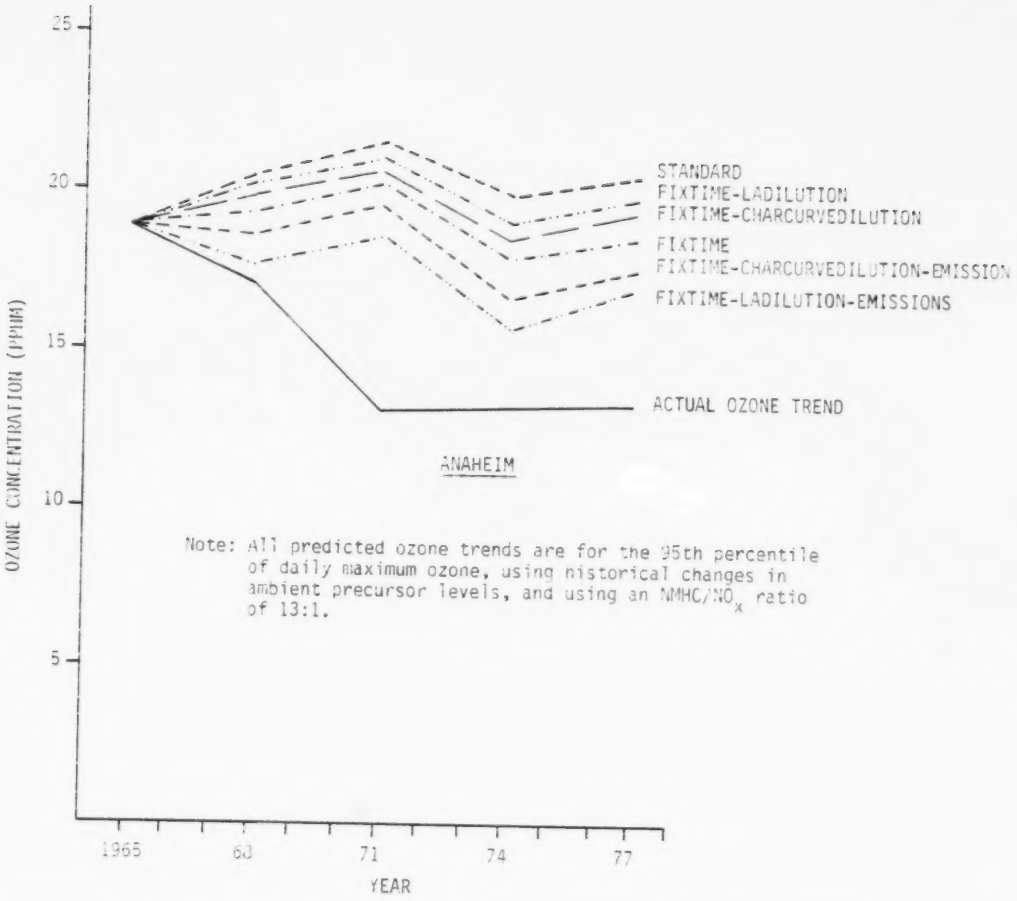

Figure 20. Sensitivity of predicted ozone trends at Anaheim to various EKMA simulation conditions.

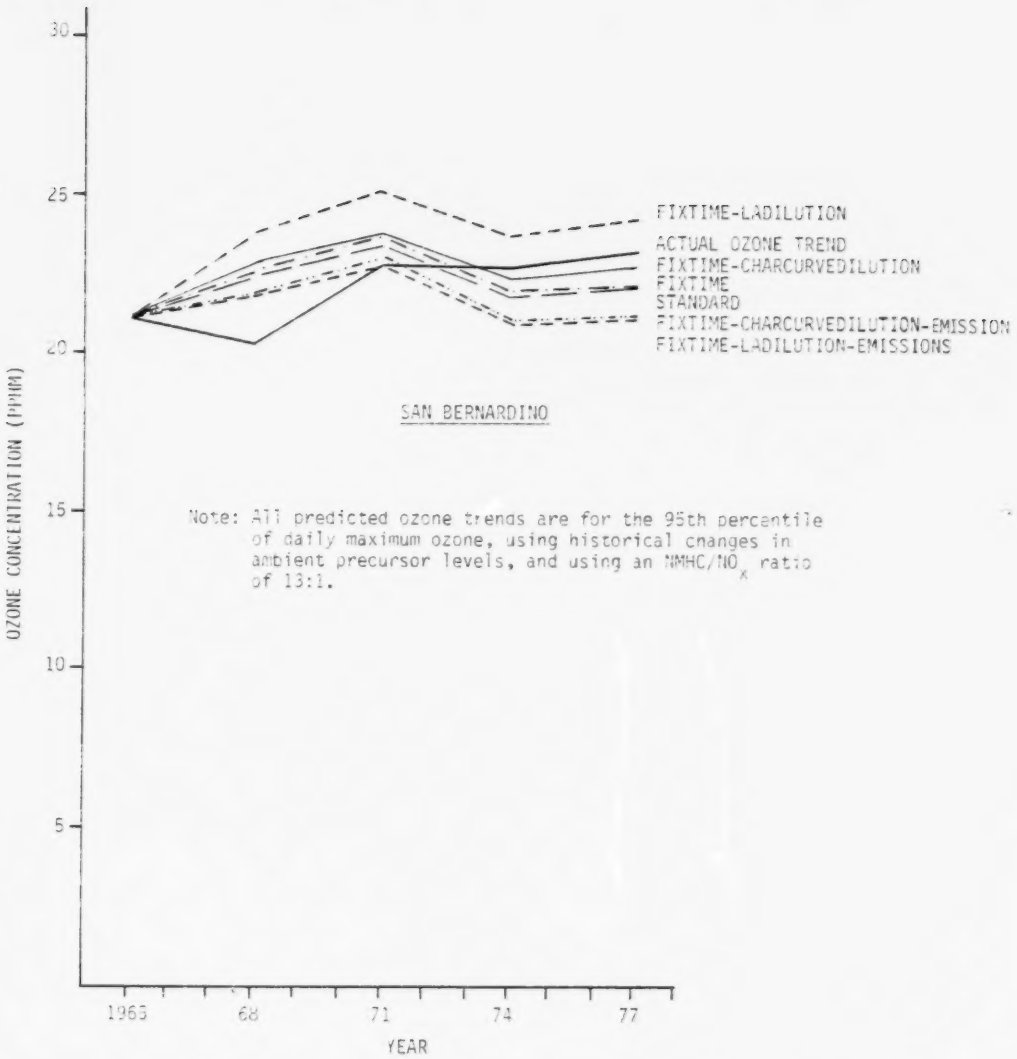

Figure 21. Sensitivity of predicted ozone trends at San Bernardino to various EKMA simulation conditions.

changes (rather than emission changes). For the sensitivity analysis we have chosen the 95th percentile index rather than the yearly maximum index because the former is a more robust measure of actual ozone trends. As discussed in Chapter 2, the predicted ozone trends based on ambient precursor changes are fairly similar to predicted ozone trends based on emission changes.

A close examination of Figures 18 through 21 leads to the following conclusions:

- The predicted ozone trends are fairly sensitive to the specific simulation conditions used to generate the EKMA isopleths. The results are sensitive to all three types of condition that are varied (i.e. time definition of ozone, dilution rate/pattern, and post 8 AM emissions).
- For this particular period in Los Angeles, the actual trends at most sites (all but San Bernardino) tend to exhibit a greater historical ozone decrease than do the predicted trends. Accordingly, for the purpose of the following conclusions, "performance" will be guaged according to the degree to which the isopleths predict decreases in historical ozone trends.
- Going from the standard isopleths to the fixed-time isopleths improves performance moderately at DOLA and Anaheim, has very little effect at San Bernardino, and worsens performance moderately at Azusa.
- Changing from the standard EKMA dilution rate to the special dilution rates (either LADILUTION or CHARCURVEDILUTION) moderately worsens performance at all four sites.
- Adding post 8 AM emissions substantially improves performance at all four sites.
- The best performance among the six types of isopleths occurs for the case of FIXTIME-LADILUTION-EMISSIONS. The FIXTIME-CHARCURVEDILUTION-EMISSIONS isopleths, those selected a priori for the final validation

tests, yield results that are very close (only slightly worse) than the results for the best performing isopleths.

Sensitivity Analyses for Various NMHC/NO_X Ratios at the Four Study Sites

Figures 22a through 22c illustrate the joint sensitivity of predicted ozone trends to two factors: EKMA simulation conditions and the NMHC/NO_X ratio. These three figures present predicted ozone trends at DOLA using the six types of isopleth for NMHC/NO_X ratios of 7:1, 13:1, and 25:1, respectively. As in Figures 18 to 21, the air quality index is the 95th percentile of daily ozone maxima, and predicted trends are based on ambient precursor changes (rather than emission changes).

Two major conclusions arise from Figures 22a through 22c. First, comparing the range of predictions within each of the three figures, it is apparent that the sensitivity of our results to the specific isopleths is greater at high and (especially) low NMHC/NO_X ratios than it is at the median (13:1) ratio. This implies that, for the type of precursor changes that occurred historically in Los Angeles (i.e. dissimilar changes in NMHC and NO_X), the selection of specific EKMA simulation conditions would be even more critical if one were examining a region with an abnormally high or low NMHC/NO_X ratio. Second, comparing the results among the three figures for each given type of isopleth, it is evident that predicted ozone is very sensitive to the NMHC/NO_X ratio for all simulations except the "STANDARD" simulation (i.e. for all the "fixed-time" simulations).

The second of these conclusions has very important implications for our study. Figure 23 shows the range in predicted ozone trends for a range in the NMHC/NO_X ratio of 7:1 to 25:1 at all four study sites, using the chosen isopleths (FIXTIME-CHARCURVEDILUTION-EMISSIONS).* It is obvious that this range in the NMHC/NO_X ratio can easily account for any of the discrepancies between predicted ozone trends and actual ozone trends. Thus, we know already that our results are extremely sensitive to the NMHC/NO_X ratio and that one type of error -- error in the NMHC/NO_X ratio -- can alone account for discrepancies

*Note that Figure 23 includes only the variance due to the range in the NMHC/NO_X ratio and does not include the variance due to the error in historical precursor trends. If the latter error were included, the range in the predicted trends would be even greater.

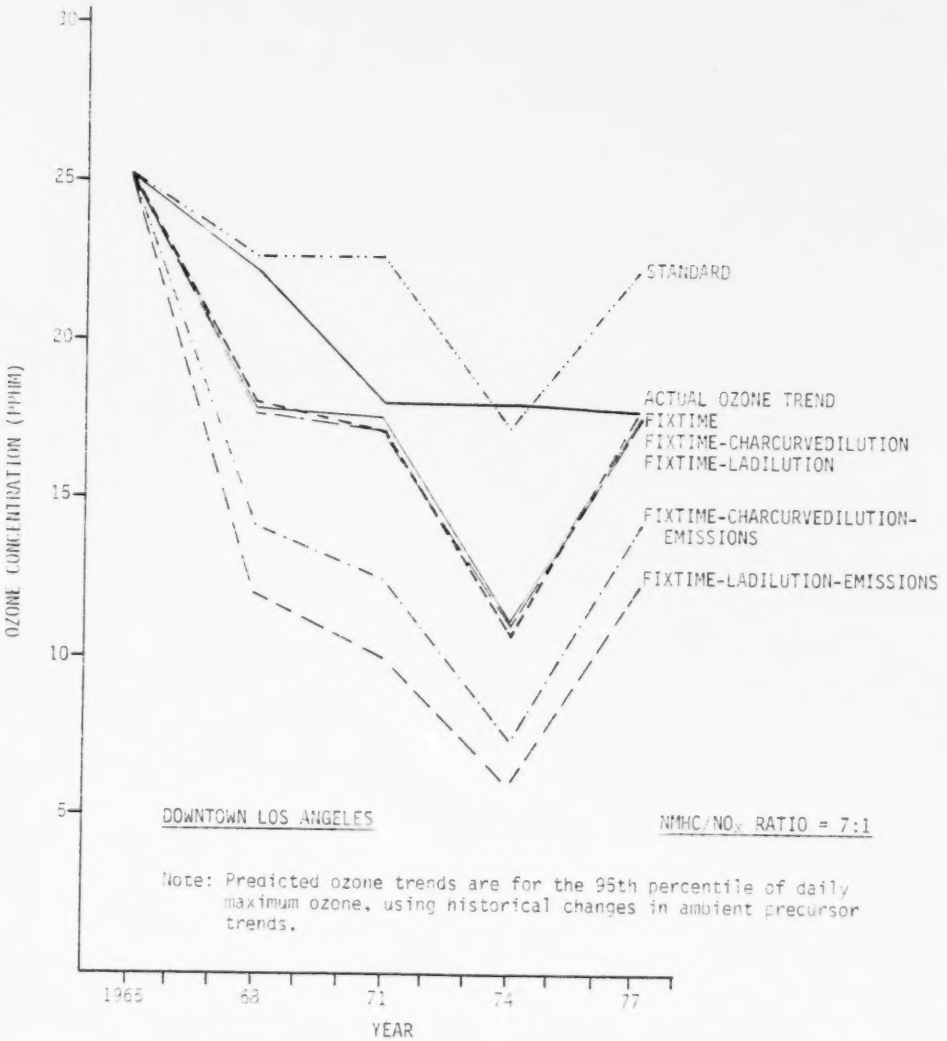

Figure 22a. Sensitivity of predicted ozone trends at DOLA to various EKMA simulation conditions for an $NMHC/NO_x$ ratio of 7:1.

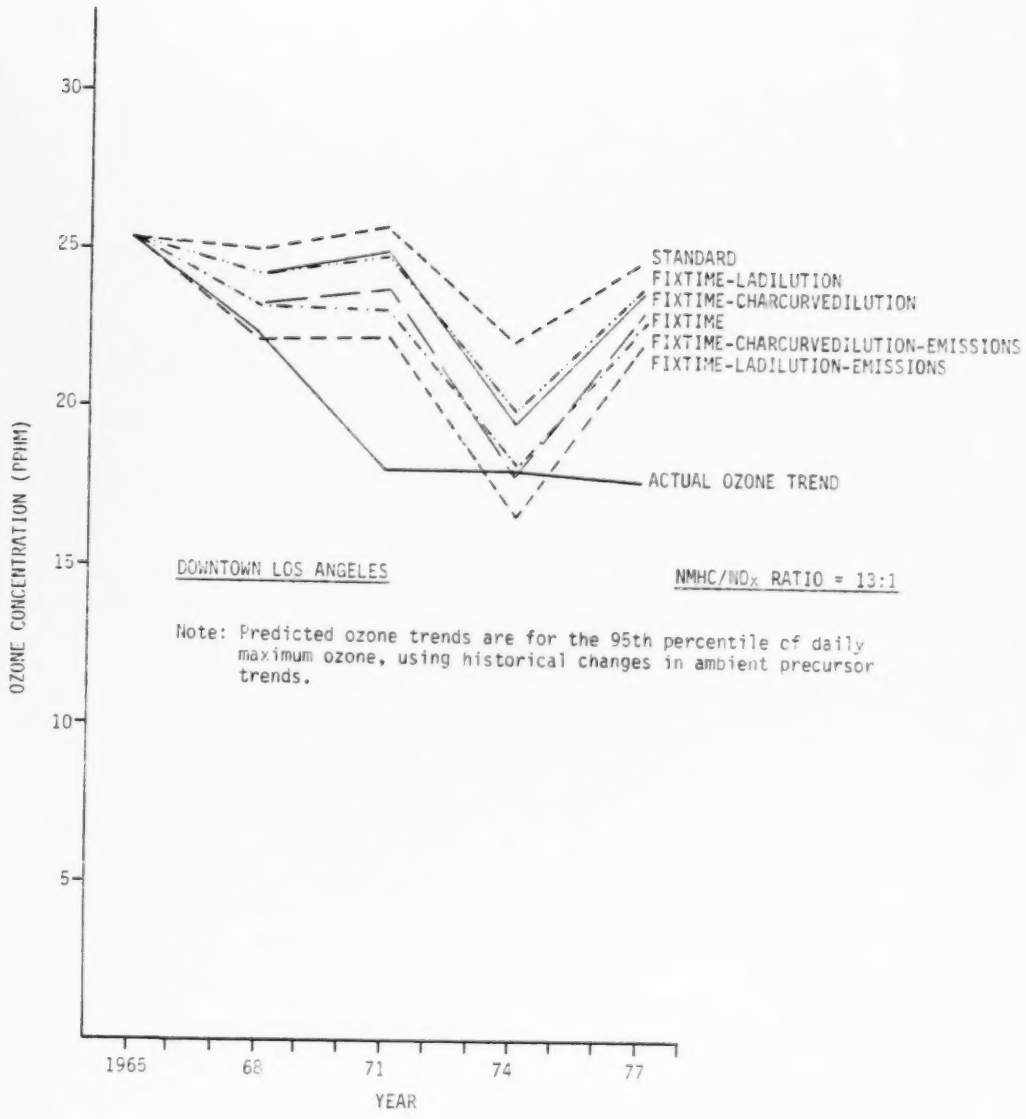

Figure 22b. Sensitivity of predicted ozone trends at DOLA to various EKMA simulation conditions for an NMHC/NO_x ratio of 13:1.

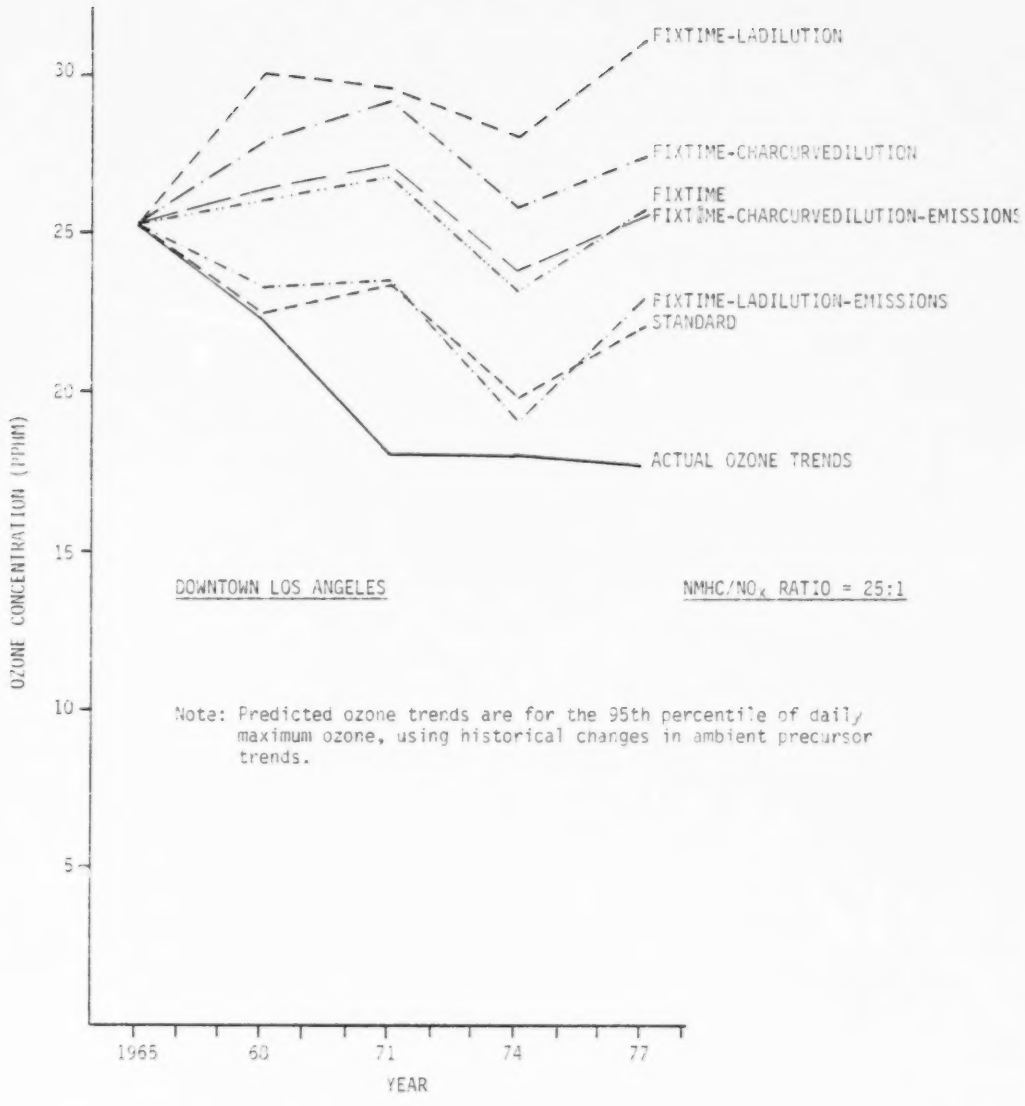

Figure 22c. Sensitivity of predicted ozone trends at DOLA to various EKMA simulation conditions for an $NMHC/NO_x$ ratio of 25:1.

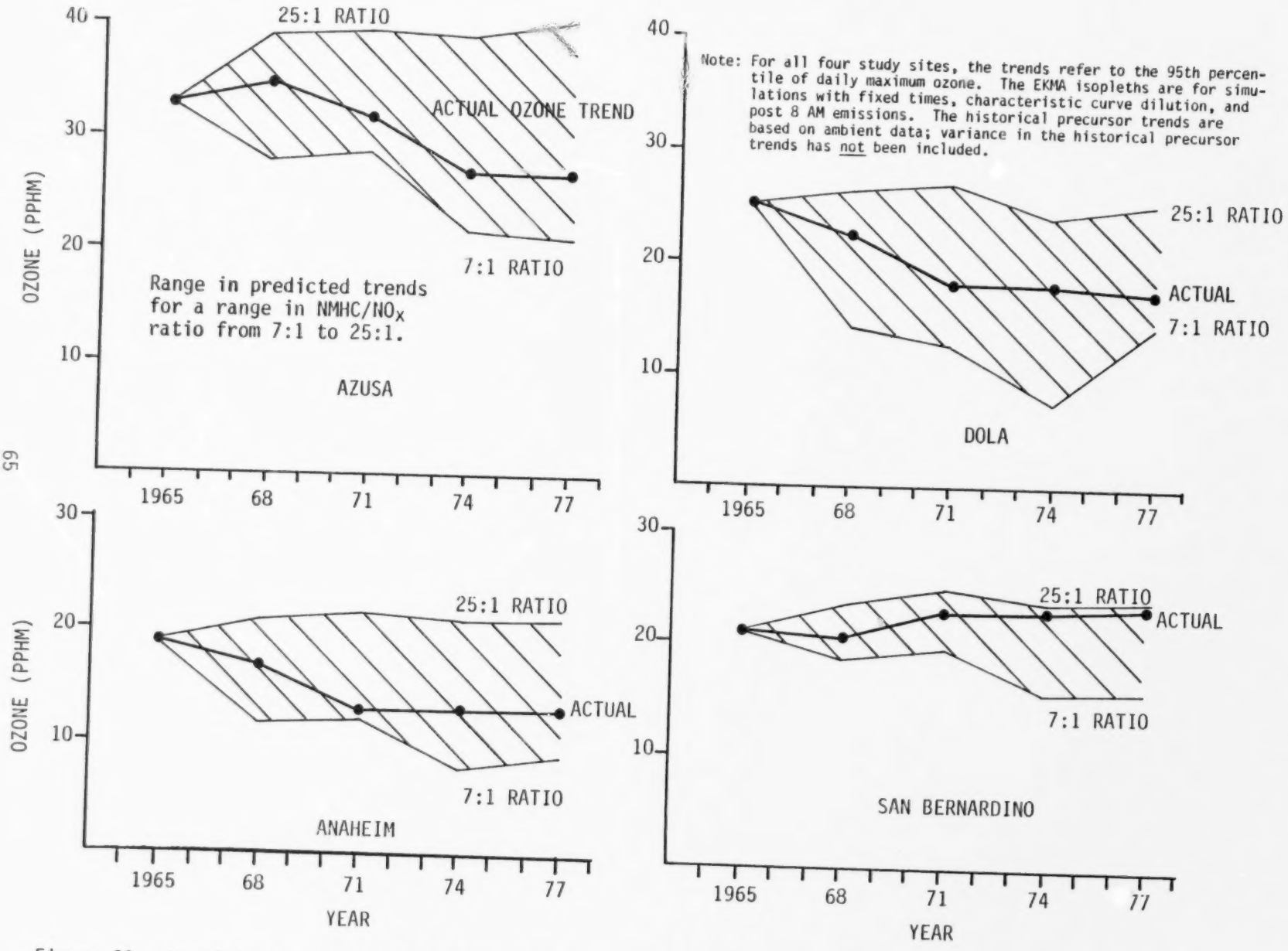

Figure 23. Sensitivity of predicted ozone trends to the range in the NMHC/NO_x ratio at all four study sites.

between observed and predicted ozone trends.

Bearing this conclusion in mind, we will conduct the isopleth validation tests (in the next Chapter) under a very stringent set of assumptions. Specifically, we will conduct the tests using only our best guess NMHC/NO_x ratio (13:1) and only the single chosen EKMA simulation conditions (characteristic curve dilution with post 8 AM emissions). If the isopleth method performs well under this very restrictive test, it will be an especially favorable reflection on the EKMA method. If the isopleth method does not perform well, we know that variance in the NMHC/NO_x ratio is one factor that alone could account for the disagreement. Sensitivity of the results to selection of appropriate EKMA simulation conditions might also be a significant factor accounting for observed discrepancies.

Sensitivity Analyses for Basinwide Maximum Ozone

Similar to the validation at the four individual study sites, the validation for basinwide maximum ozone will use EKMA simulation conditions including the 150 to 600 meter mixing height change, "characteristic curve" dilution, and post 8 AM emissions. Since we are dealing with basinwide maximum ozone rather than ozone at a fixed monitoring site, the ozone value will be taken as the maximum value over a 10-hour irradiation rather than the value at a fixed irradiation time. Figure 24 shows predicted trends based on this set of isopleths (CHARCURVEDILUTION-EMISSIONS) as well as for the standard EKMA isopleths for basinwide maximum ozone (STANDARD). Both sets of predictions are based on an NMHC/NO_x ratio of 13:1 and on ambient precursor changes (rather than emission changes). Unlike the case of the "fixed-time" isopleths used at the individual study sites, the predicted ozone trends based on basinwide isopleths do not appear to be sensitive to the specific EKMA simulation conditions.

Figure 25 shows the sensitivity of the results (using CHARCURVE-DILUTION-EMISSIONS isopleths) to the NMHC/NO_x ratio, for a range of the ratio from 7:1 to 25:1. As was the case with the analysis at the four individual monitoring sites, the predictions are sensitive to the initial NMHC/NO_x ratio. The sensitivity, however, is not quite as great as it was for the "fixed-time" isopleths used at the individual monitoring sites.

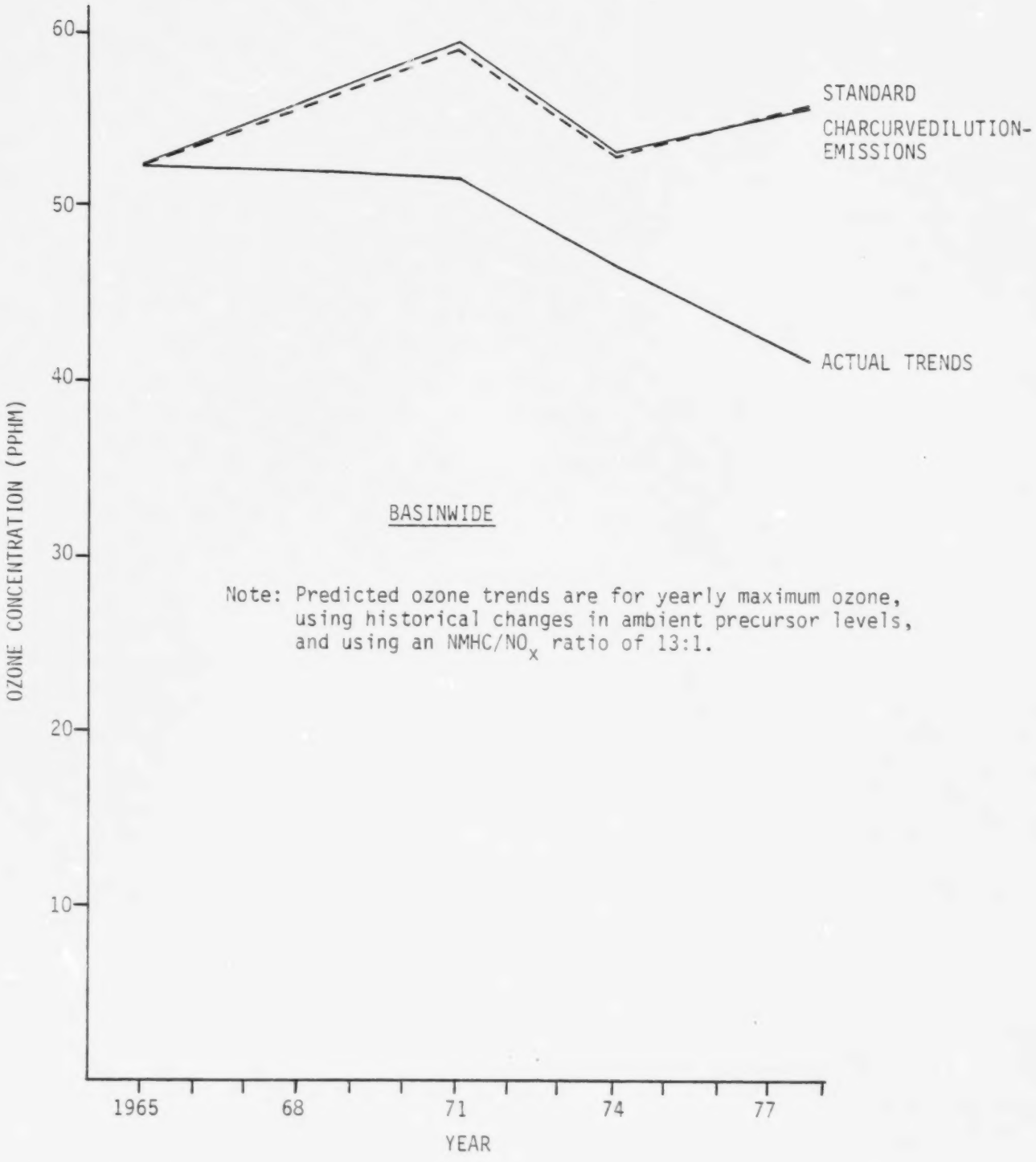

Figure 24. Sensitivity of predicted trends for yearly basinwide maximum ozone to two alternative EKMA simulation conditions.

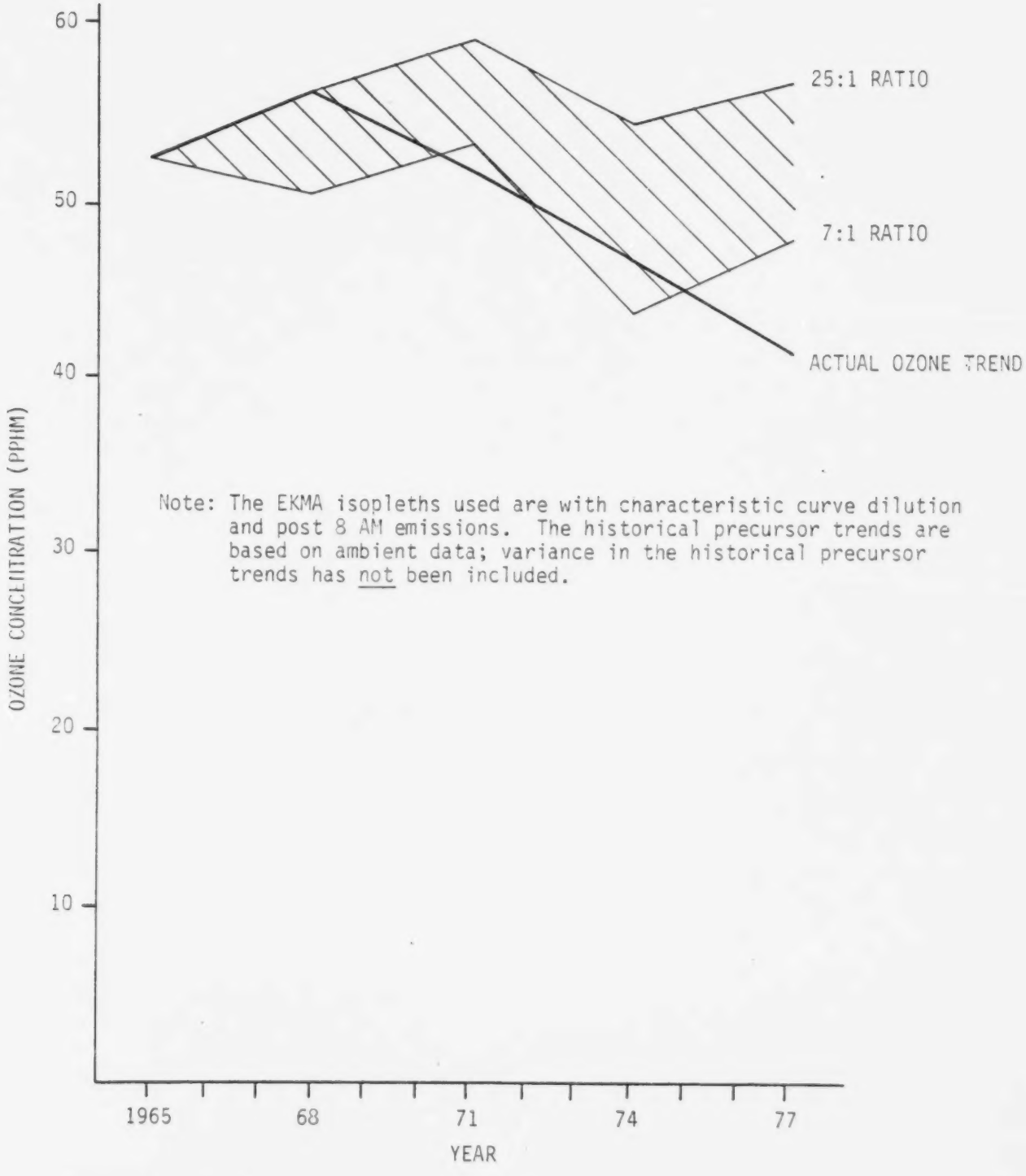

Figure 25. Sensitivity of predicted trends for yearly basinwide maximum ozone to the range in the NMHC/NO_x ratio.

CHAPTER 5

VALIDATION OF THE EKMA ISOPLETH METHOD

This chapter describes the Los Angeles validation studies of the EKMA isopleth method. Historical precursor trends (either emission trends or ambient precursor trends) and the EKMA isopleth model are used to predict historical ozone trends; these predicted ozone trends are then compared to actual ozone trends. The validation studies are conducted for basinwide maximum ozone as well as for two ozone air quality indices (yearly maximum concentration and 95th percentile of daily maximum concentrations) at four individual monitoring sites (Azusa, DOLA, Anaheim, and San Bernardino).

After the results of the validation studies are presented, this chapter discusses potential explanations for disagreements between predicted and actual ozone trends and describes implications of our study with respect to future applications of EKMA. As a postscript to the chapter, we also discuss the controversey surrounding the recent lack of improvement in ozone trends for Los Angeles.

VALIDATION PROCEDURE

The EKMA validation tests proceed as follows. The base period for the validation study is 1964-1966. The two base period inputs to the EKMA model are the initial ozone concentration (see Table 9 page 43) and the base period NMHC/NO_x ratio (a value of 13:1 is used, see Chapter 4). Using the base period inputs and historical precursor trends (either the emission trends in Table 3 on page 23 or the ambient precursor trends in Tables 4 to 7 on pages 27 to 30), predictions are made of historical ozone trends with the graphical EKMA technique for each subsequent 3-year period -- 1967-1969, 1970-1972, 1973-1975, and 1976-1978. The predicted ozone trends are then compared to actual ozone trends (the latter are listed in Table 9 page 43).

Figure 26 illustrates the graphical EKMA technique for the case of 95th percentile of daily maximum ozone at Azusa, with historical precursor trends based on the emissions data. The base period point (1964-1966,

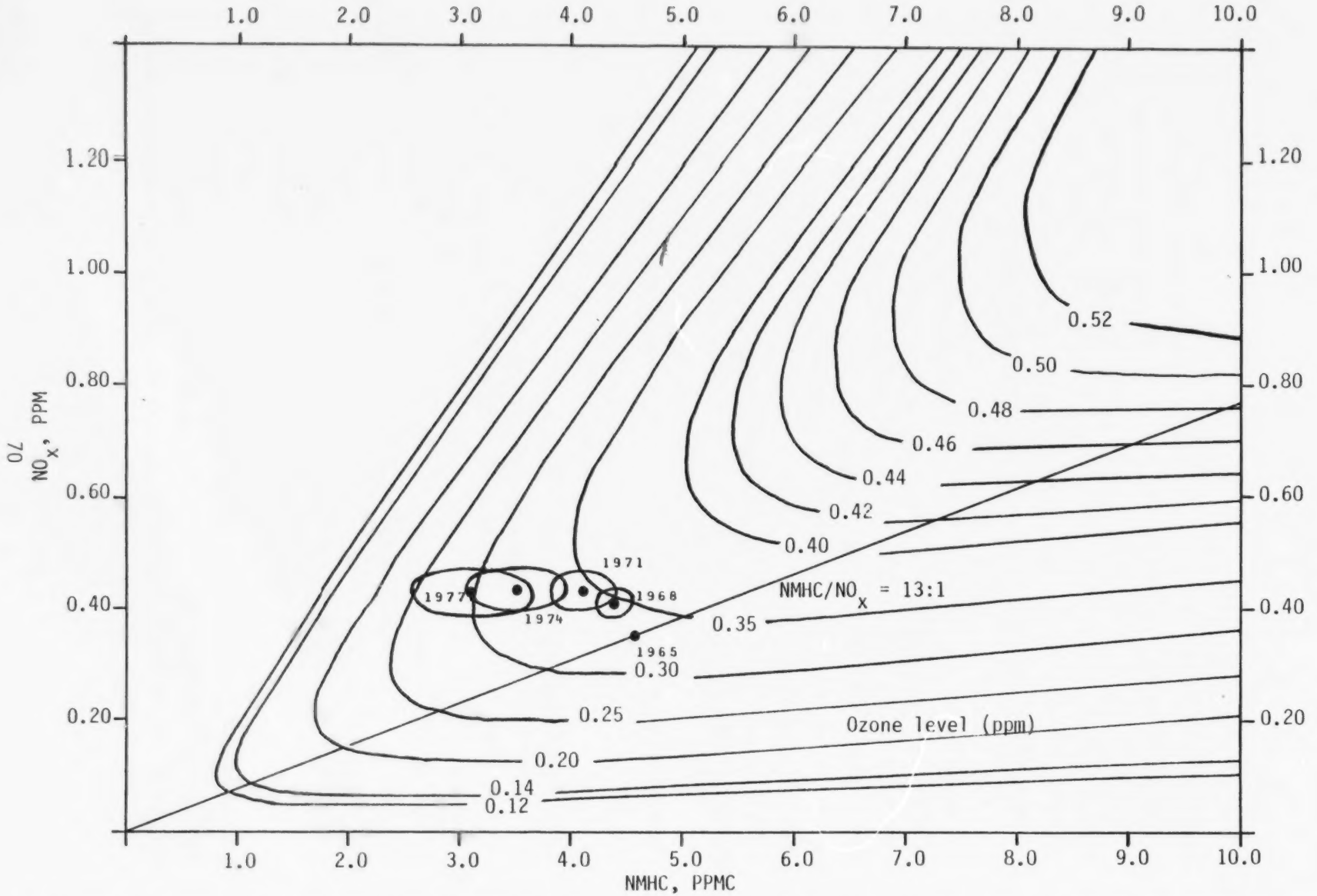

Figure 26. Use of EKMA to predict historical ozone trends at Azusa (95th percentile of daily maximum ozone, with predictions based on emission trends).

labelled "1965") is determined by the intersection of the 13:1 ratio line with the ozone value for the base period (33.3 pphm). The location of the points for the four subsequent 3-year periods (labelled "1968", "1971", "1974", and "1977") are found by factoring the NMHC and NO_x coordinates of the base period point according to the precursor changes relative to the base period. The isopleths then yield predicted ozone values for these subsequent periods.

Error bounds are attached to both the predicted and actual ozone trends. The error bounds on predicted trends are determined from error-ellipses in the isopleth diagrams as shown in Figure 26. The size of these ellipses is based on the errors in the precursor trends (the errors in the emission trends are listed in Table 3 on page 23; the errors in the ambient precursor trends are listed in Tables 4 to 7 on pages 27 to 30). The actual ozone trends include error bounds representing the fluctuations in ozone levels produced by meteorological variance (these errors are listed in Table 10 on page 43).

The reader should be reminded that variance in the base period NMHC/NO_x ratio introduces another error in the predicted ozone trends. As discussed in Chapter 4, the predicted ozone trends are so sensitive to the base period NMHC/NO_x ratio that any of the observed discrepancies between predicted and actual ozone trends could be explained by errors in the NMHC/NO_x ratio. The figures presented in this chapter represent a rather stringent test of the EKMA isopleth method because we have not included errors in the base period NMHC/NO_x ratio. The effects of such errors were illustrated quantitatively in Chapter 4 and will be discussed again near the end of this chapter.

As another reminder, we note that the EKMA isopleths employed here represent standard EKMA conditions except for the addition of post 8 AM emissions and the use of a "characteristic curve" dilution pattern with a diurnal mixing height change from 150 meters at 8 AM to 600 meters at 5 PM. Also, at the four individual study sites, the ozone value in the EKMA isopleths represents the ozone concentration at fixed irradiation times rather than maximum ozone over the entire irradiation period.

VALIDATION STUDIES BASED ON EMISSION TRENDS

This section presents the results of the EKMA validation studies using emission trend data (rather than ambient precursor trend data) as the basis for predicting historical ozone trends. Figures 27 through 30 present the validation tests for the 95th percentile of daily maximum ozone at the four study locations; Figures 31 through 34 present results for yearly maximum ozone at the four sites. Figure 35 illustrates the results for basinwide maximum ozone.

Considering the severity of the test conditions (in the sense that we have not included potential errors in the NMHC/NO_x ratio), the results of the validation studies are not poor. In most cases, the predicted and actual ozone trends agree within the error bounds representing errors in the emission trends and meteorological variance in the actual ozone trends. There is, however, a disturbing general pattern that predicted ozone trends do not show the historical decreases exhibited by actual ozone trends. This pattern occurs for all air quality indices and sites except San Bernardino. The discrepancy is particularly severe for the 95th percentile of daily maxima at DOLA, the 95th percentile of daily maxima at Anaheim, the yearly maximum at Azusa, and the yearly maximum at DOLA.

VALIDATION STUDIES BASED ON AMBIENT PRECURSOR TRENDS

Figures 36 to 44 correspond to Figures 27 to 35, except the predicted ozone trends are now based on ambient precursor trends (rather than emission trends). Examining these figures, we reach conclusions that are very similar to our findings in the previous section. Again, the results of the validation studies are not poor considering the stringency of the test conditions. Most of the error bars on the predicted and actual trends overlap. Again, however, there is the disturbing general tendency for predicted ozone trends to underestimate decreases in actual ozone trends at all sites except San Bernardino. This discrepancy is particularly great for the 95th percentile of daily maxima at Azusa, the 95th percentile of daily maxima at Anaheim, the yearly maximum at Azusa, the yearly maximum at DOLA, and the basinwide yearly maximum.

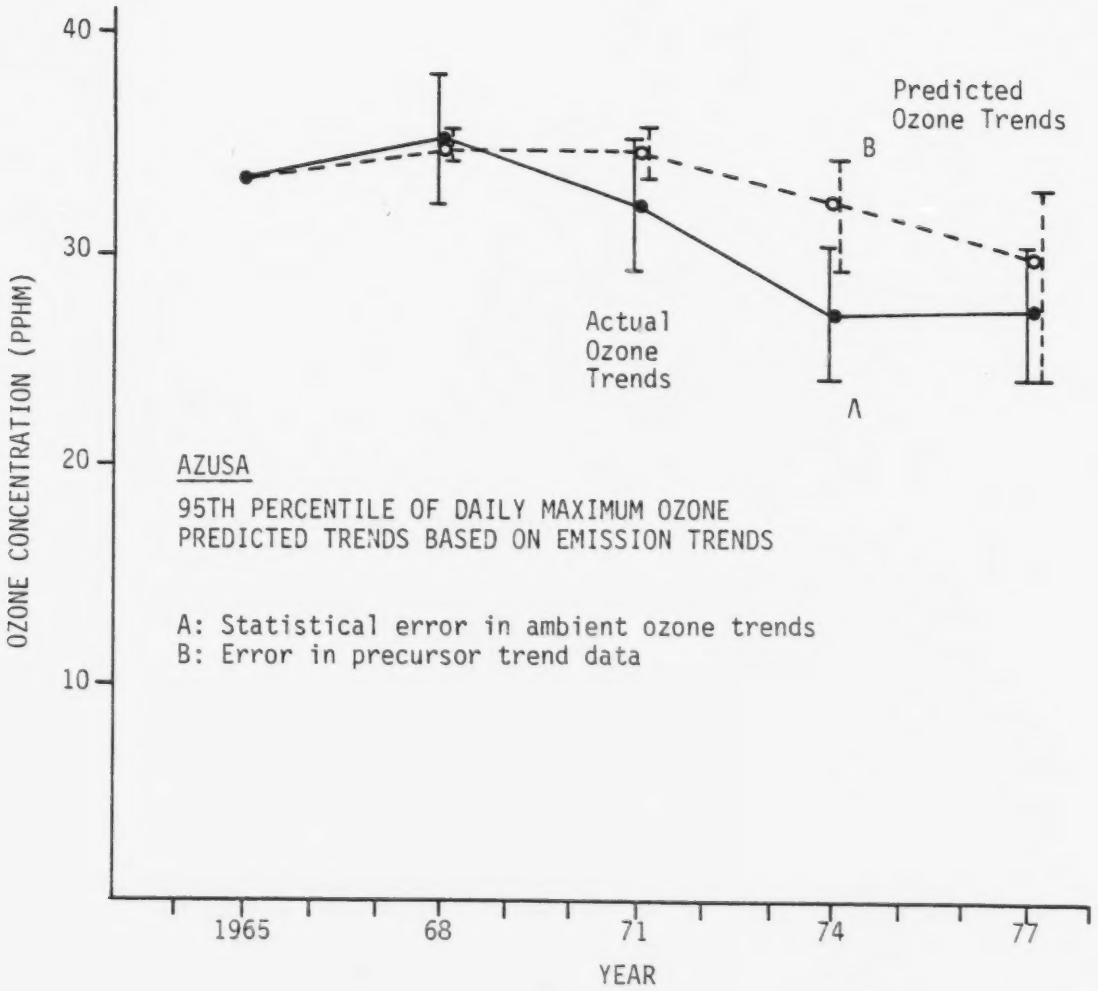

Figure 27. Results of the validation studies for the 95th percentile of daily maximum ozone at Azusa, using emission trends to derive predicted ozone trends.

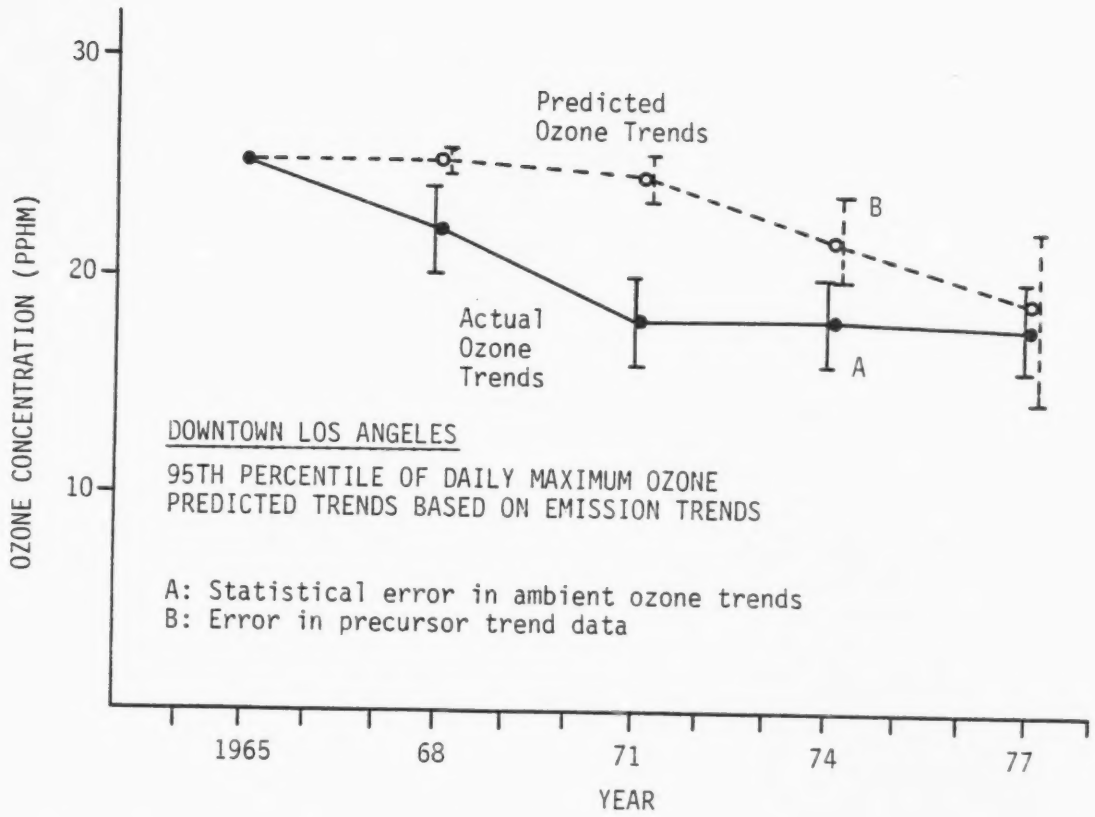

Figure 28. Results of the validation studies for the 95th percentile of daily maximum ozone at Downtown Los Angeles, using emission trends to derive predicted ozone trends.

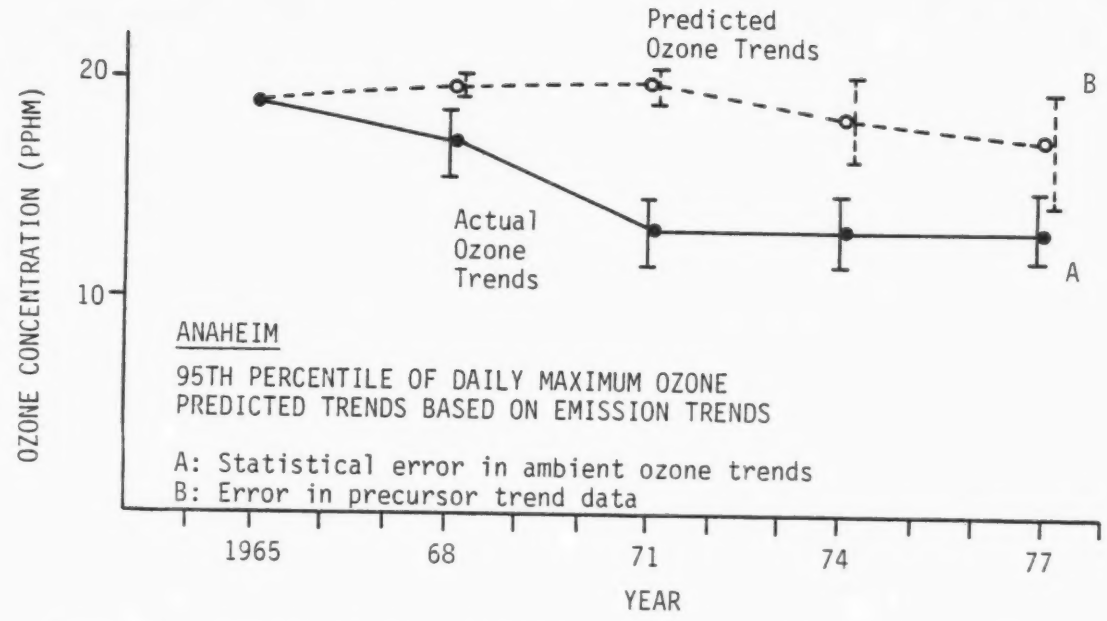

Figure 29. Results of the validation studies for the 95th percentile of daily maximum ozone at Anaheim, using emission trends to derive predicted ozone trends.

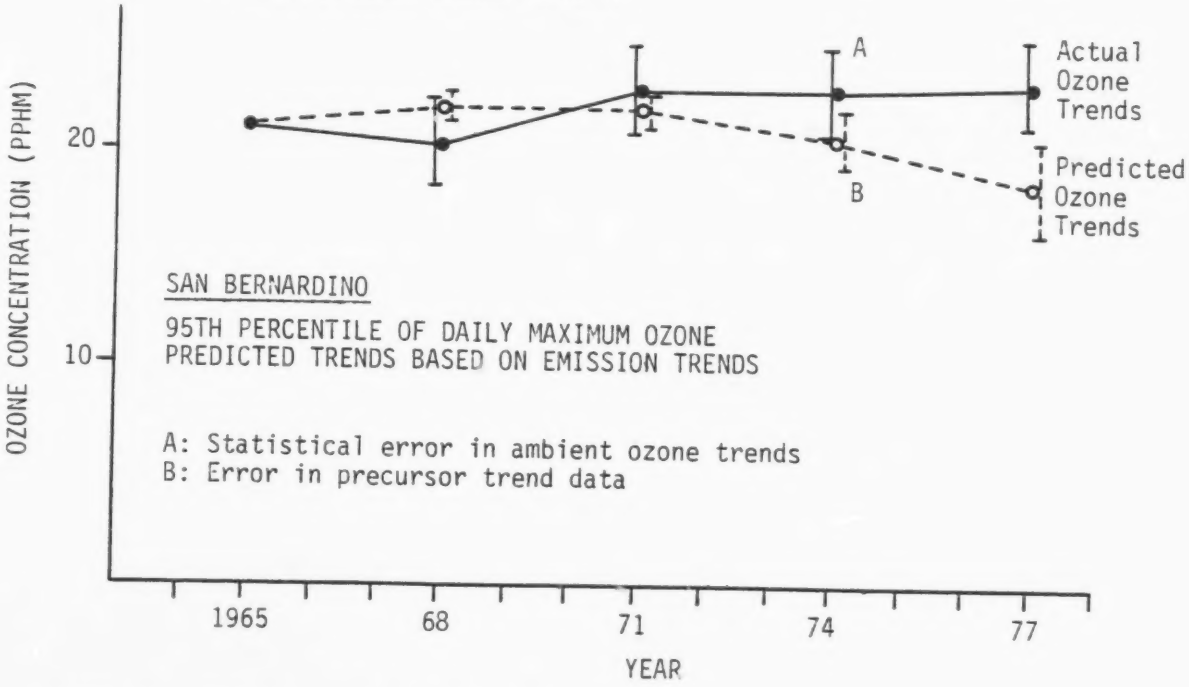

Figure 30. Results of the validation studies for the 95th percentile of daily maximum ozone at San Bernardino, using emission trends to derive predicted ozone trends.

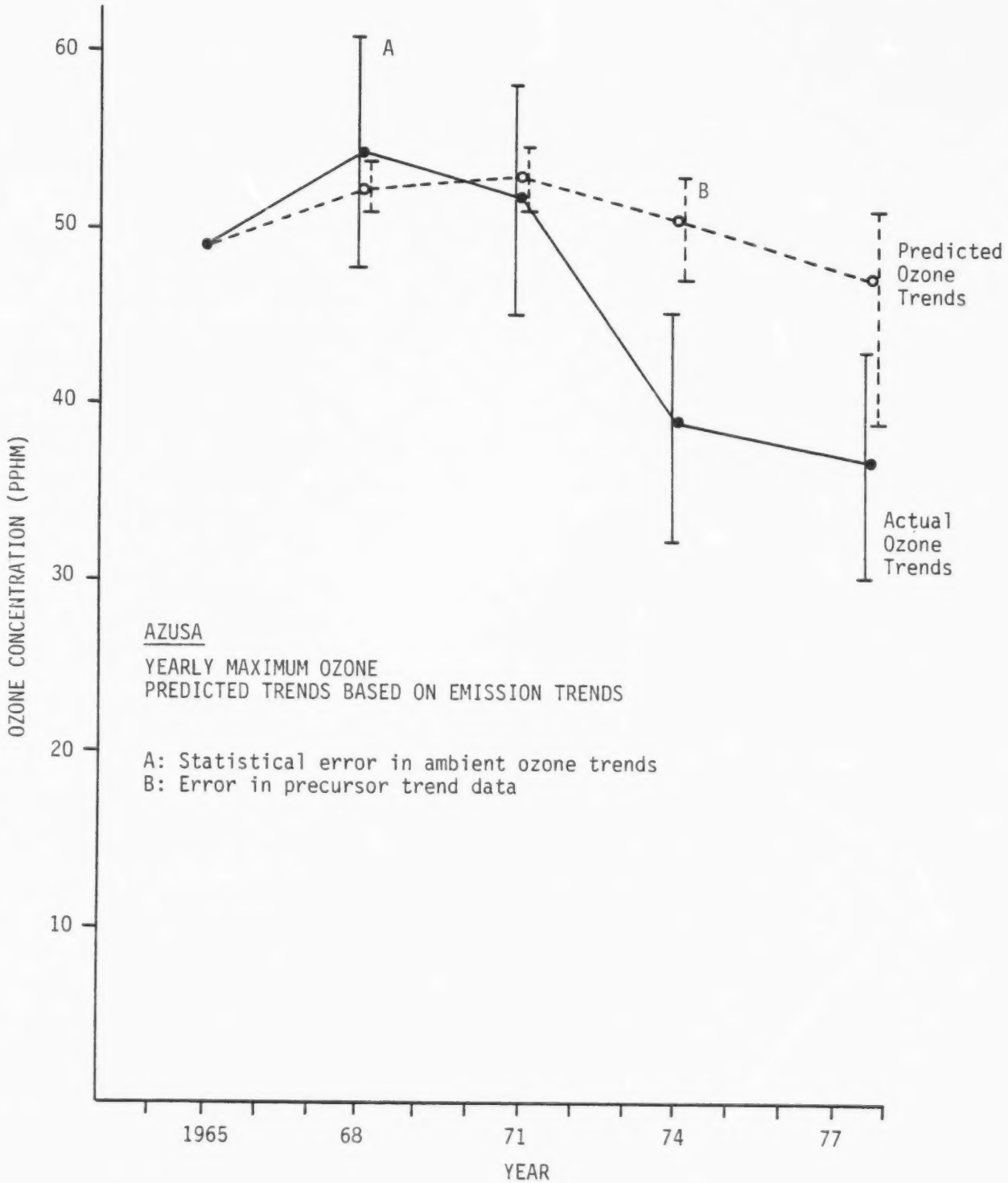

Figure 31. Results of the validation studies for yearly maximum ozone at Azusa, using emission trends to derive predicted ozone trends.

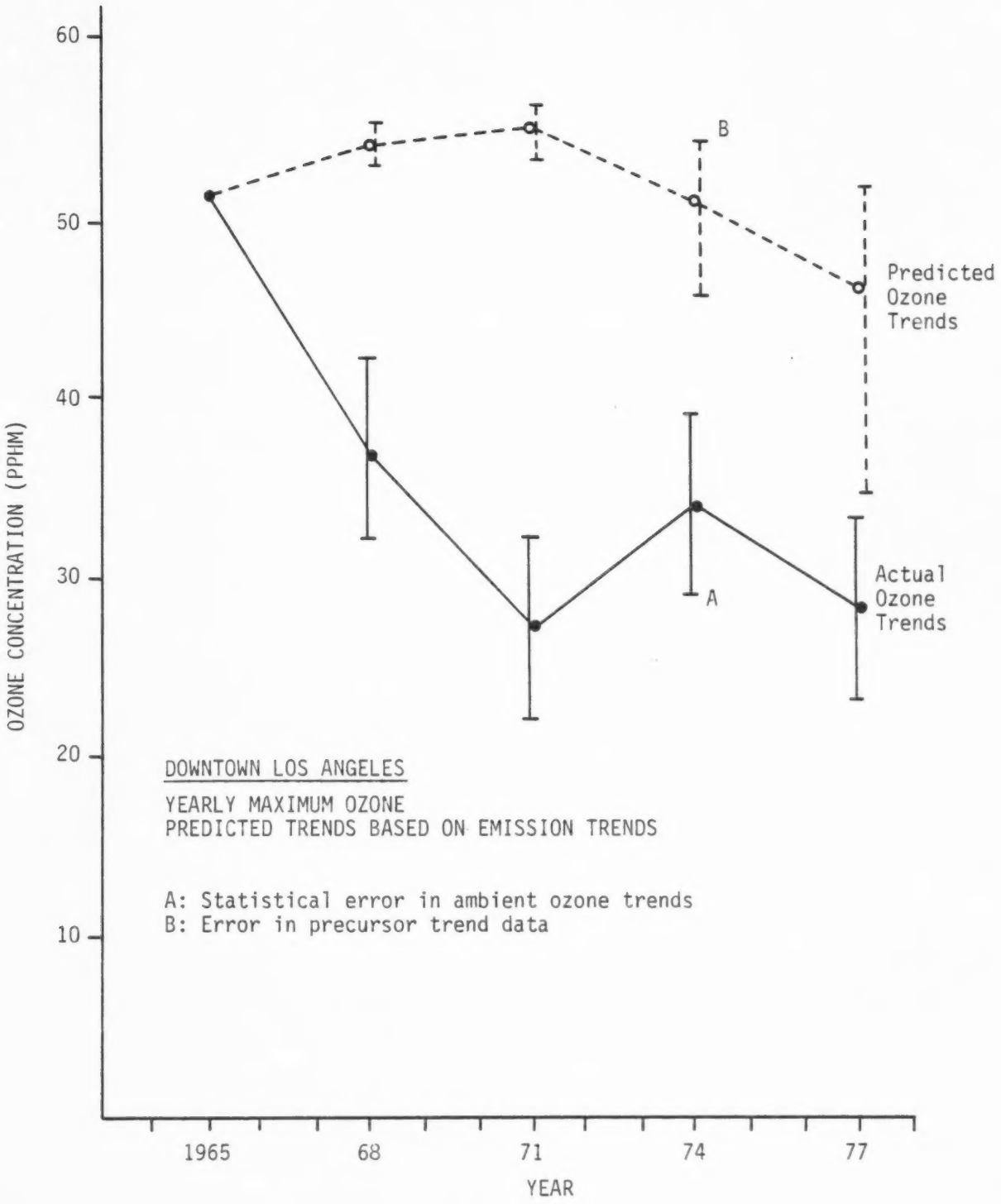

Figure 32. Results of the validation studies for yearly maximum ozone at Downtown Los Angeles, using emission trends to derive predicted ozone trends.

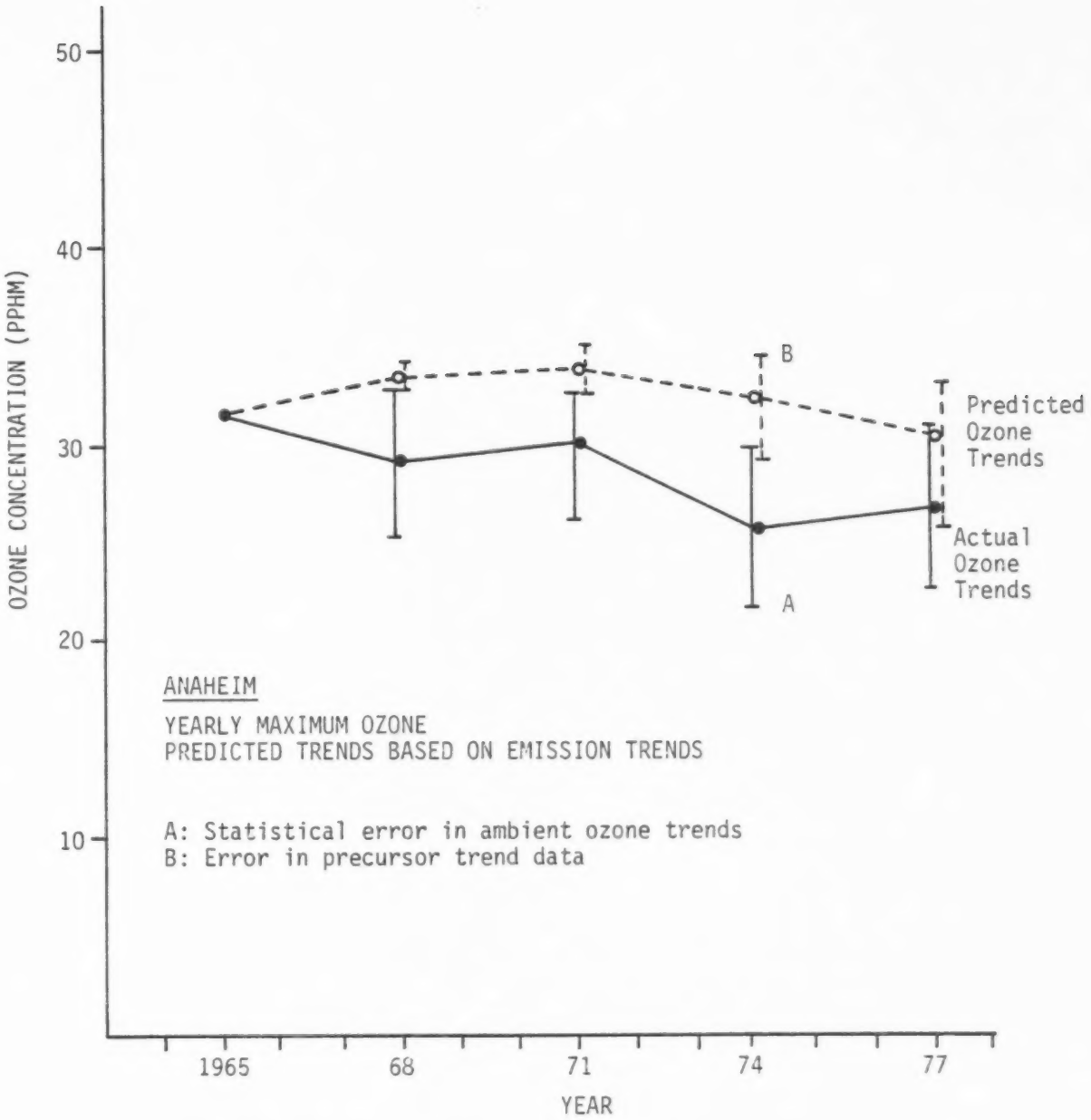

Figure 33. Results of the validation studies for yearly maximum ozone at Anaheim, using emission trends to derive predicted ozone trends.

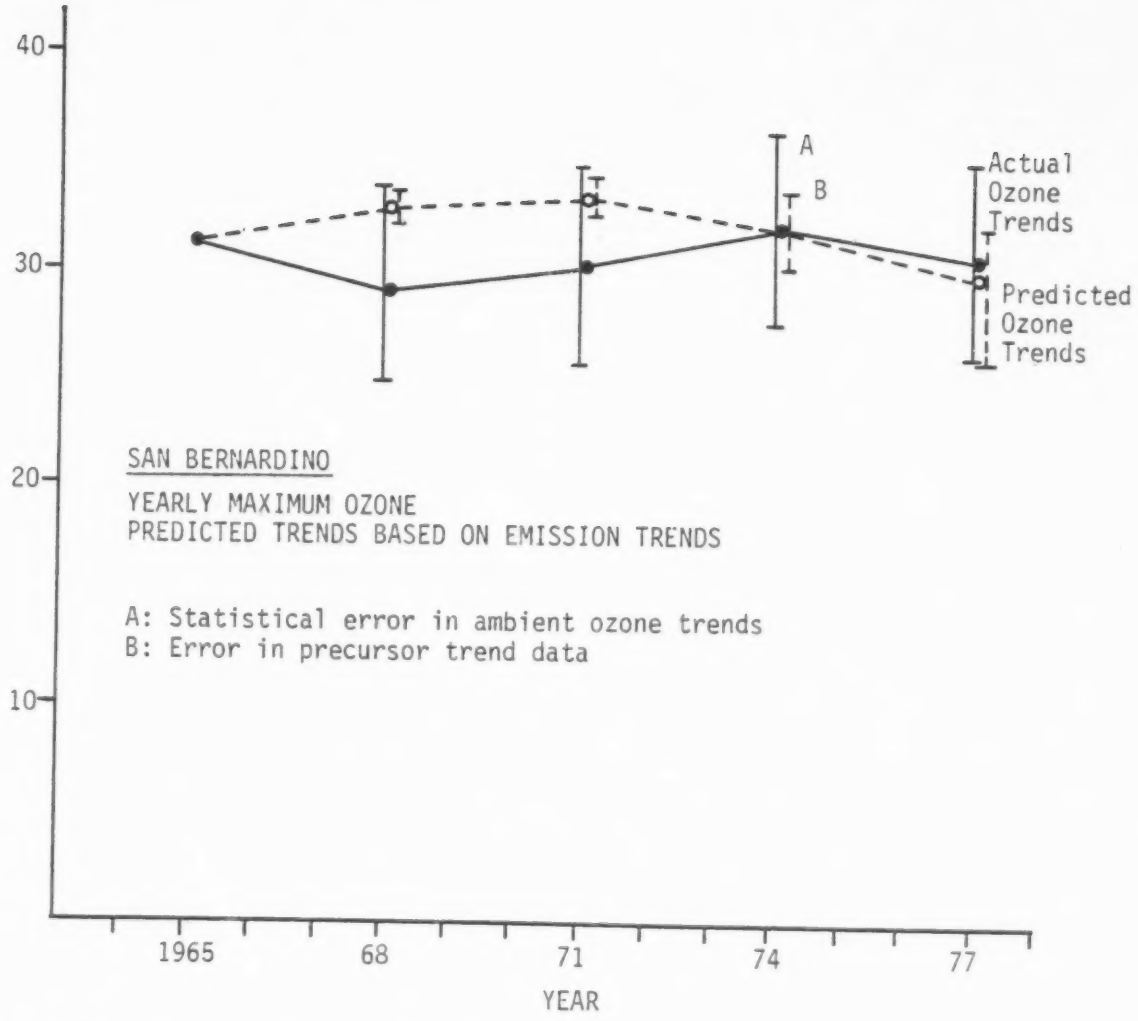

Figure 34. Results of the validation studies for yearly maximum ozone at San Bernardino, using emission trends to derive predicted ozone trends.

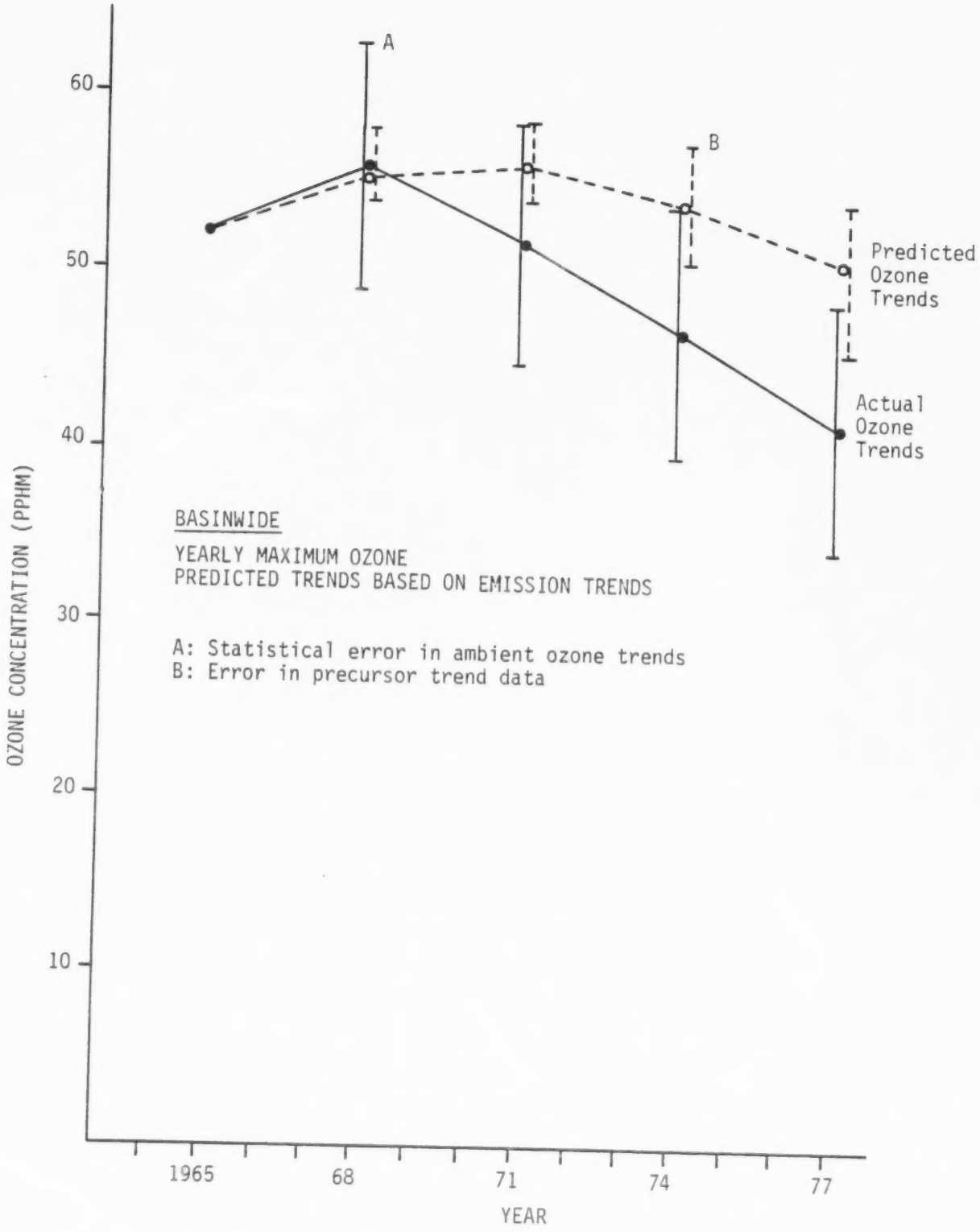

Figure 35. Results of the validation studies for basinwide yearly maximum ozone, using emission trends to derive predicted ozone trends.

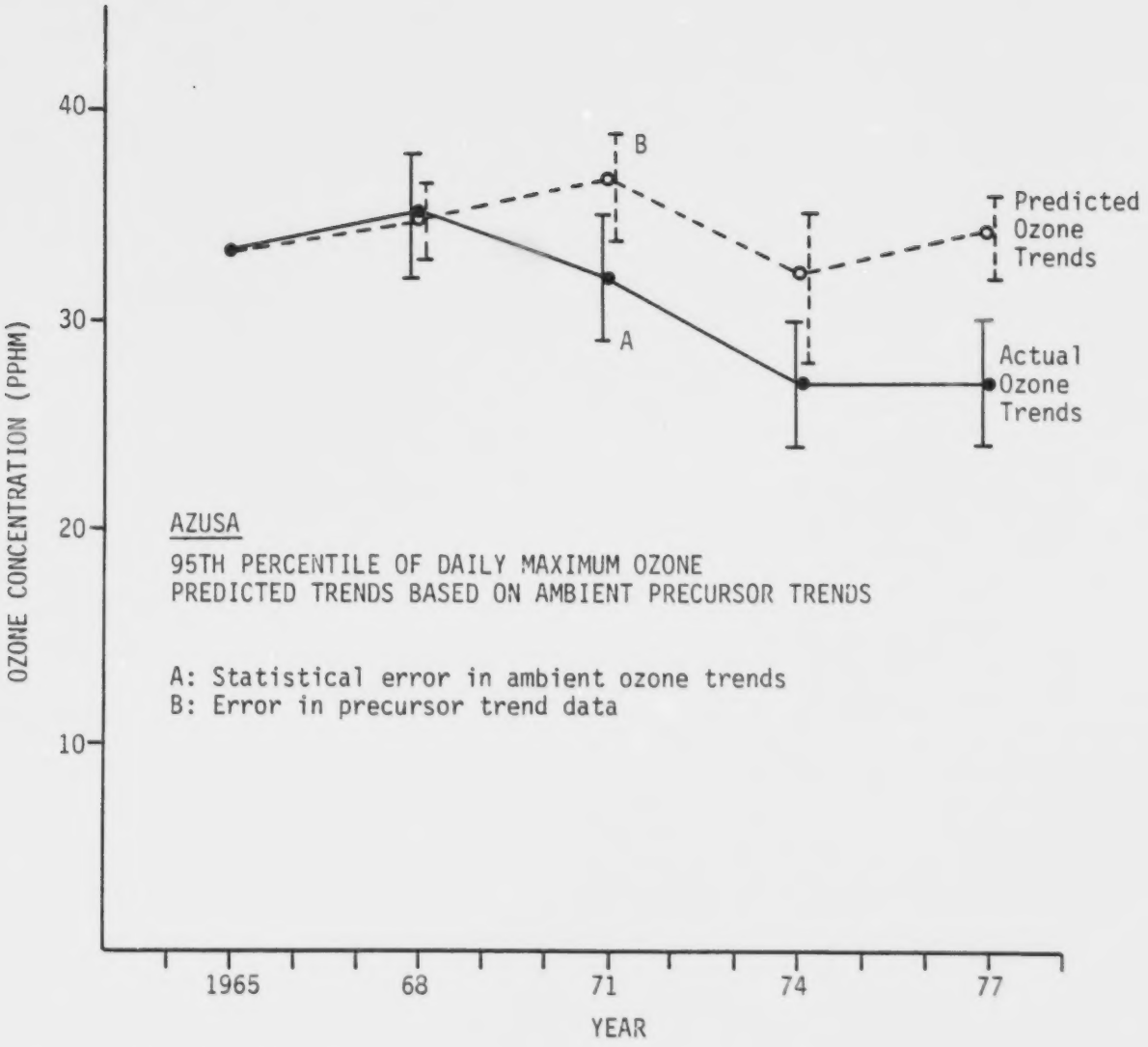

Figure 36. Results of the validation studies for the 95th percentile of daily maximum ozone at Azusa, using ambient precursor trends to derive predicted ozone trends.

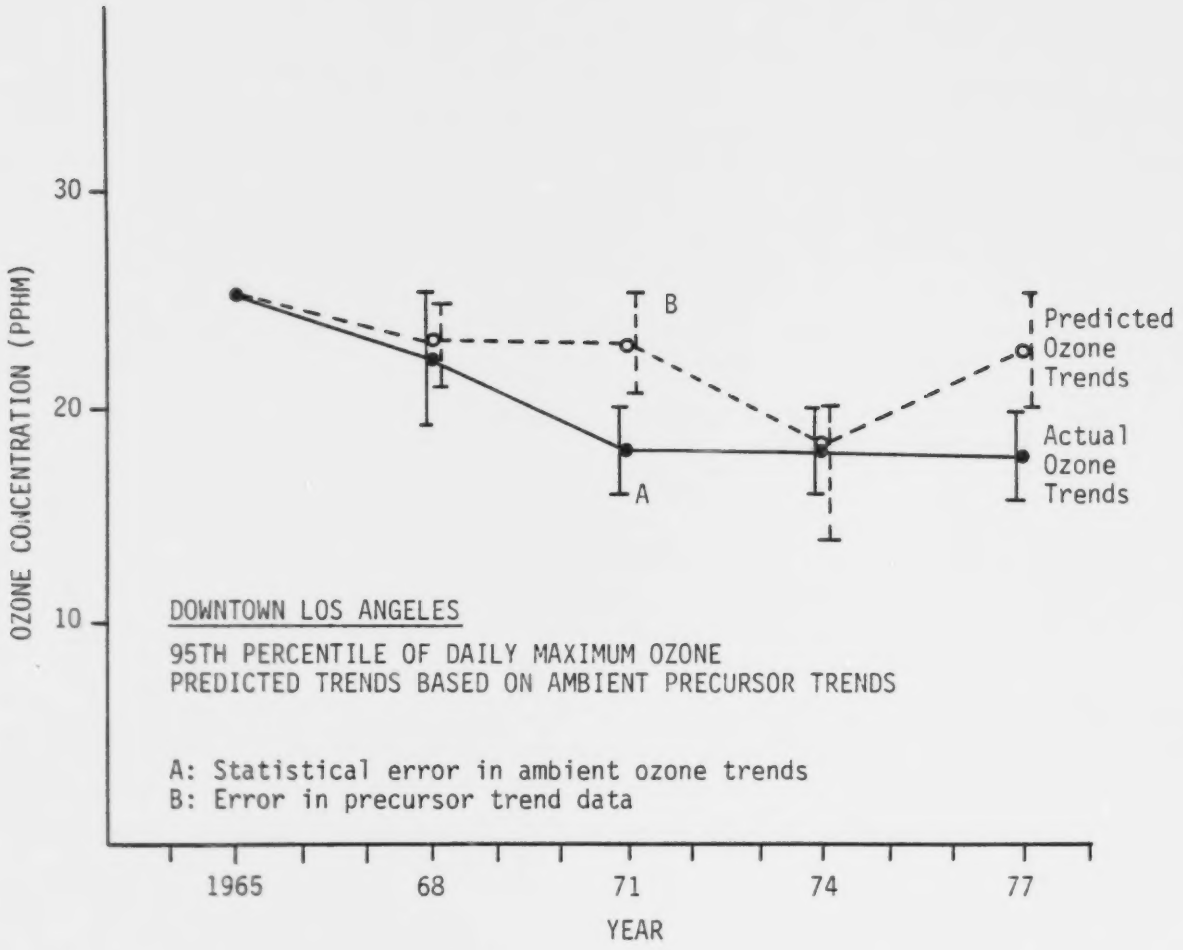

Figure 37. Results of the validation studies for the 95th percentile of daily maximum ozone at Downtown Los Angeles, using ambient precursor trends to derive predicted ozone trends.

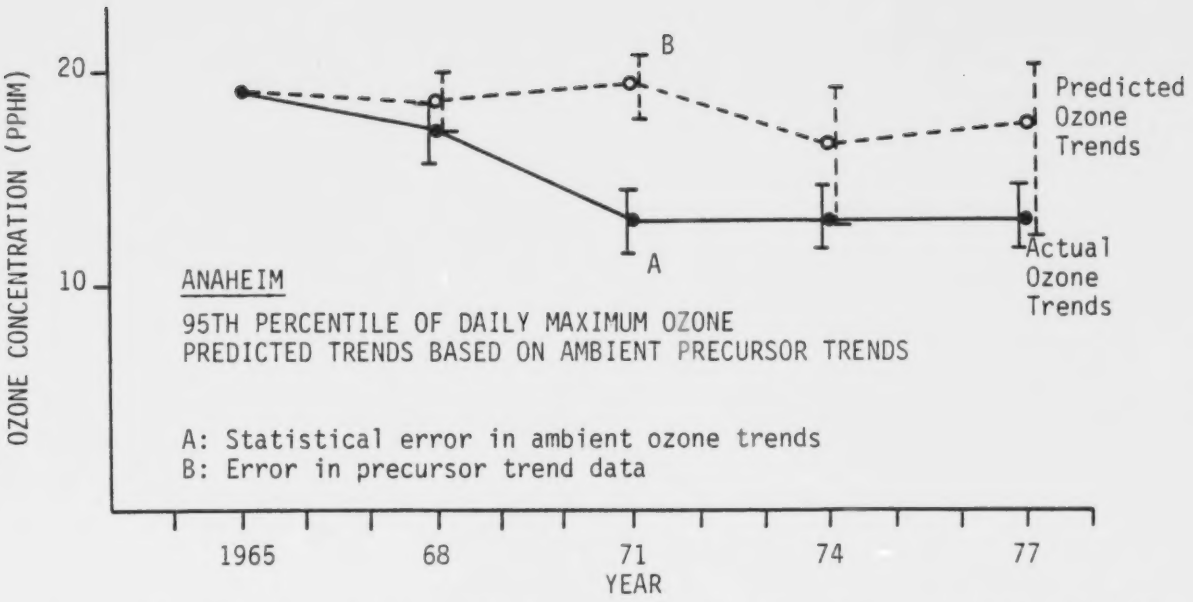

Figure 38. Results of the validation studies for the 95th percentile of daily maximum ozone at Anaheim, using ambient precursor trends to derive predicted ozone trends.

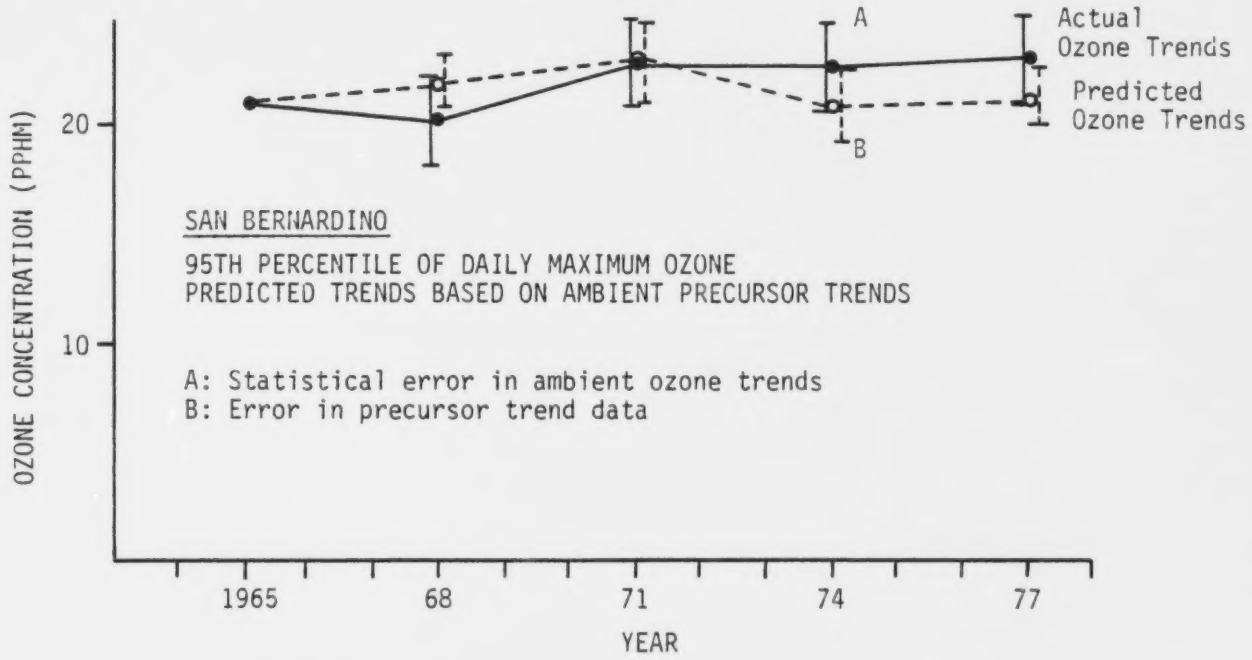

Figure 39. Results of the validation studies for the 95th percentile of daily maximum ozone at San Bernardino, using ambient precursor trends to derive predicted ozone trends.

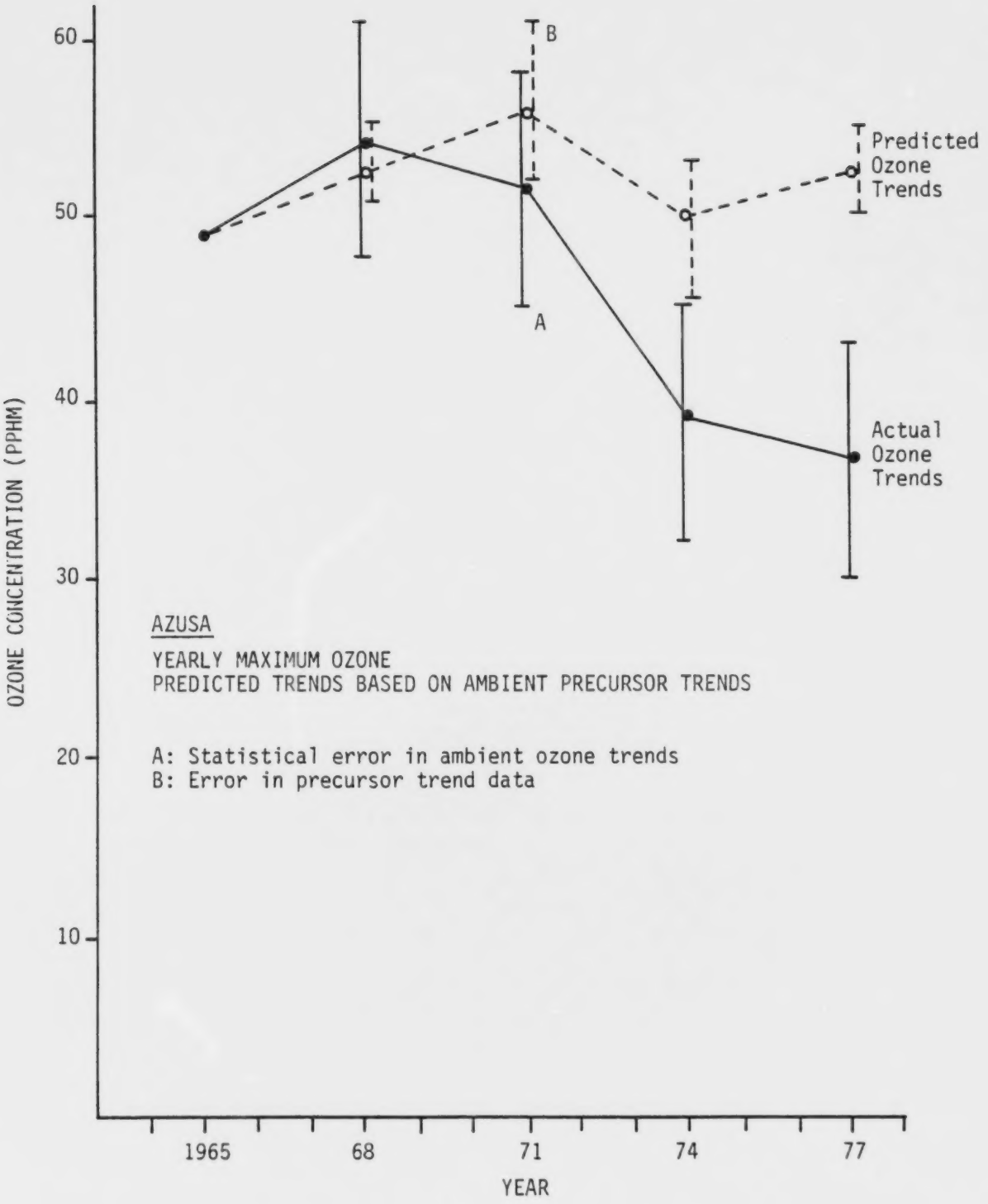

Figure 40. Results of the validation studies for yearly maximum ozone at Azusa, using ambient precursor trends to derive predicted ozone trends.

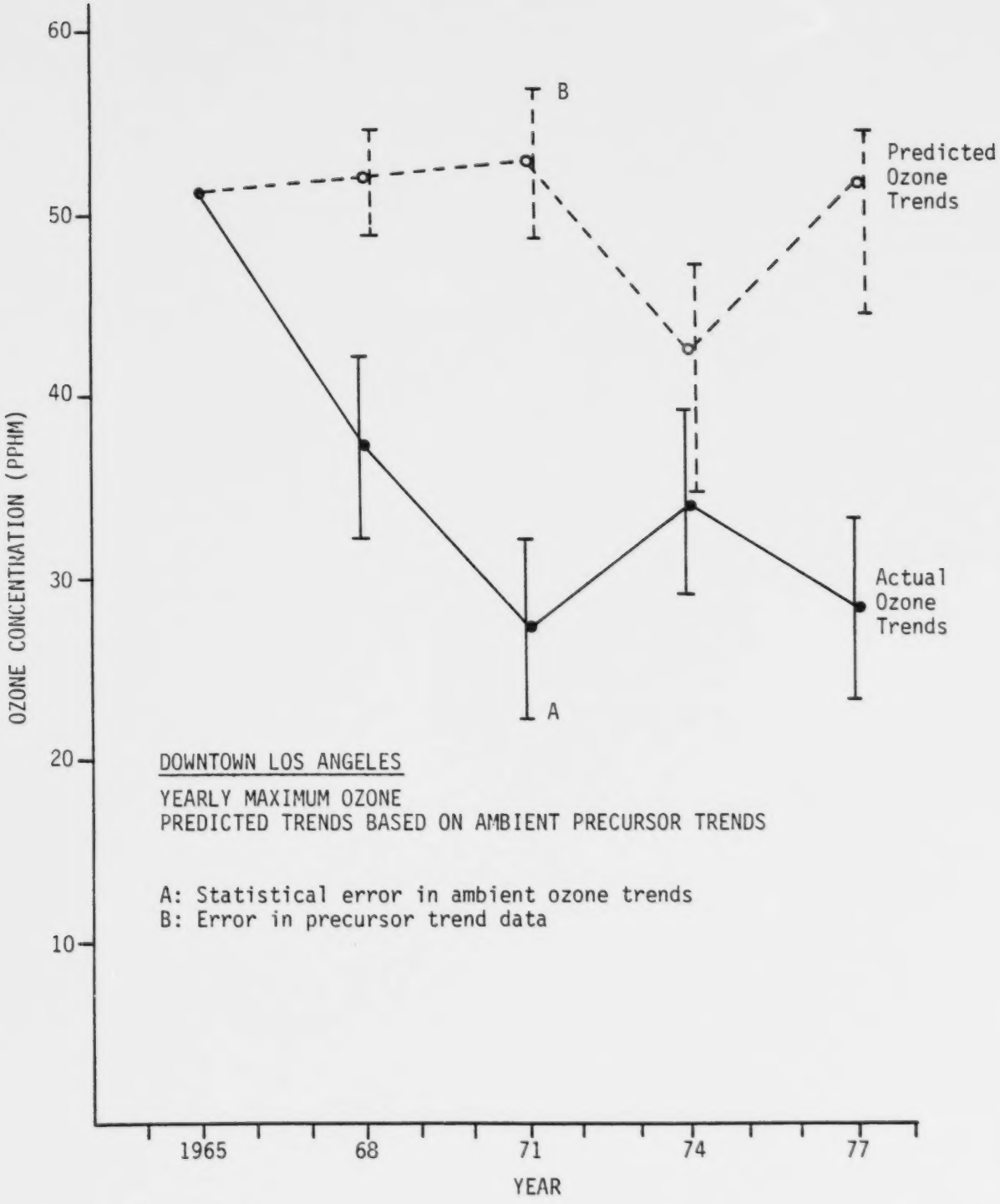

Figure 41. Results of the validation studies for yearly maximum ozone at Downtown Los Angeles, using ambient precursor trends to derive predicted ozone trends.

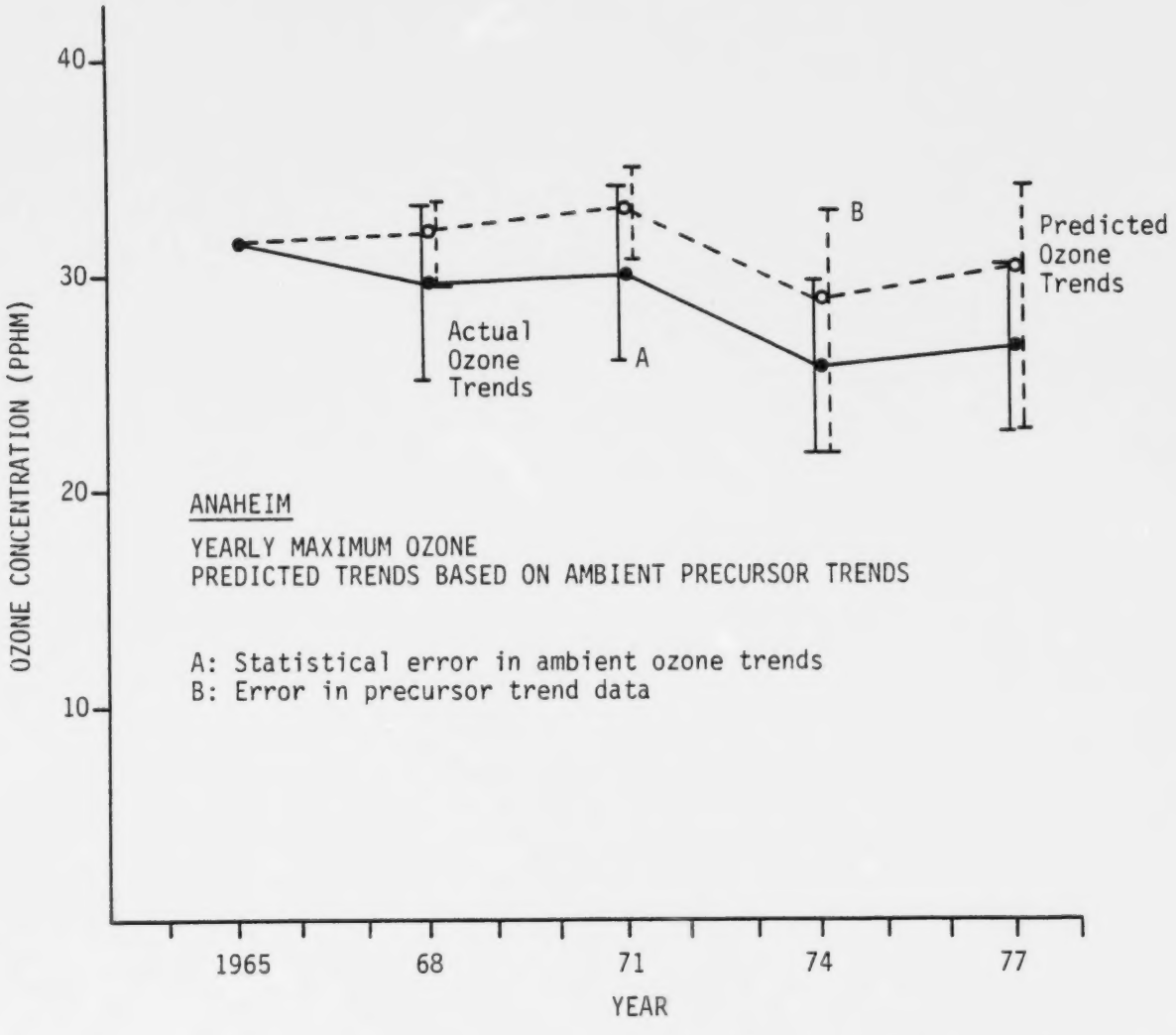

Figure 42. Results of the validation studies for yearly maximum ozone at Anaheim, using ambient precursor trends to derive predicted ozone trends.

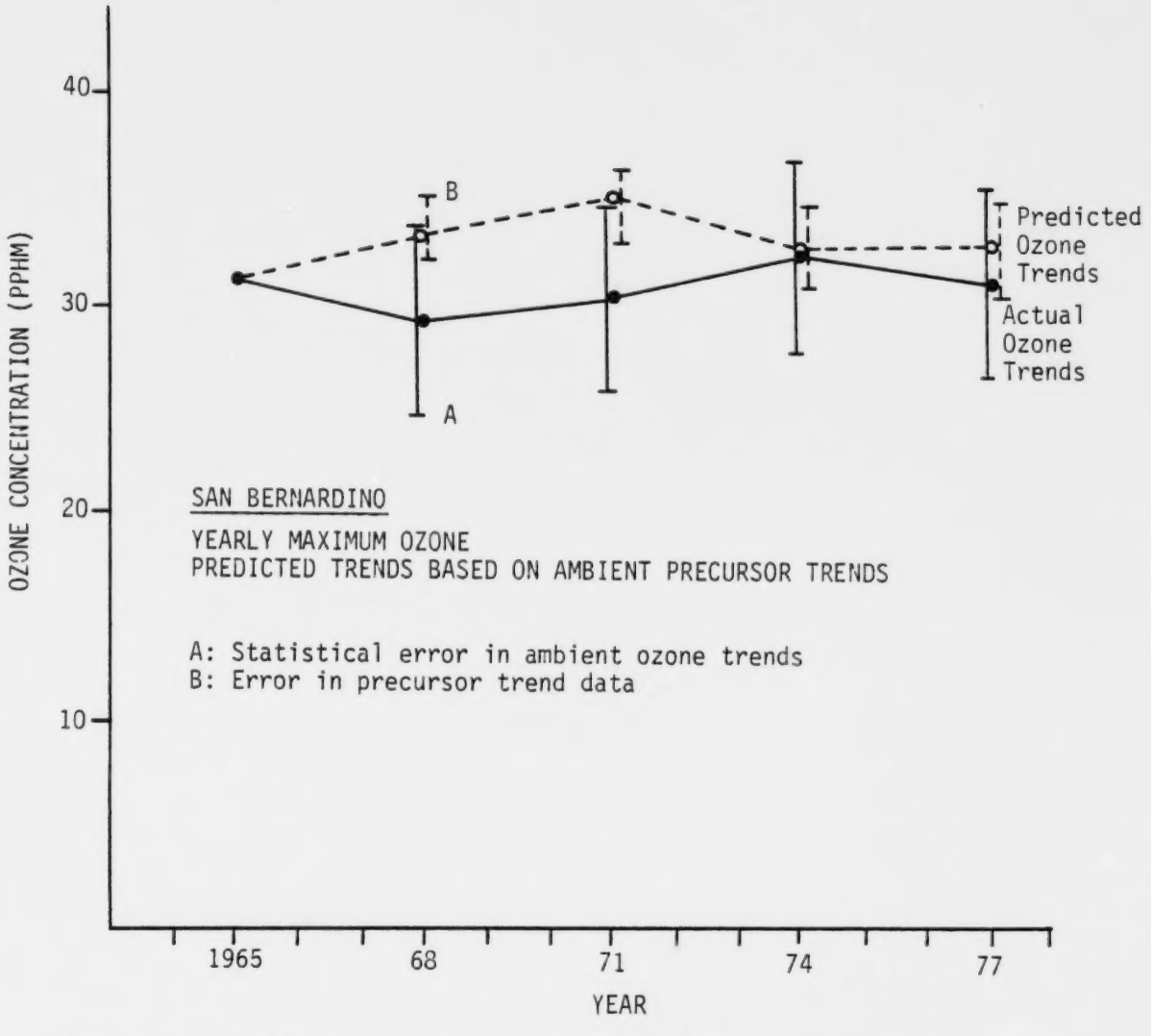

Figure 43. Results of the validation studies for yearly maximum ozone at San Bernardino, using ambient precursor trends to derive predicted ozone trends.

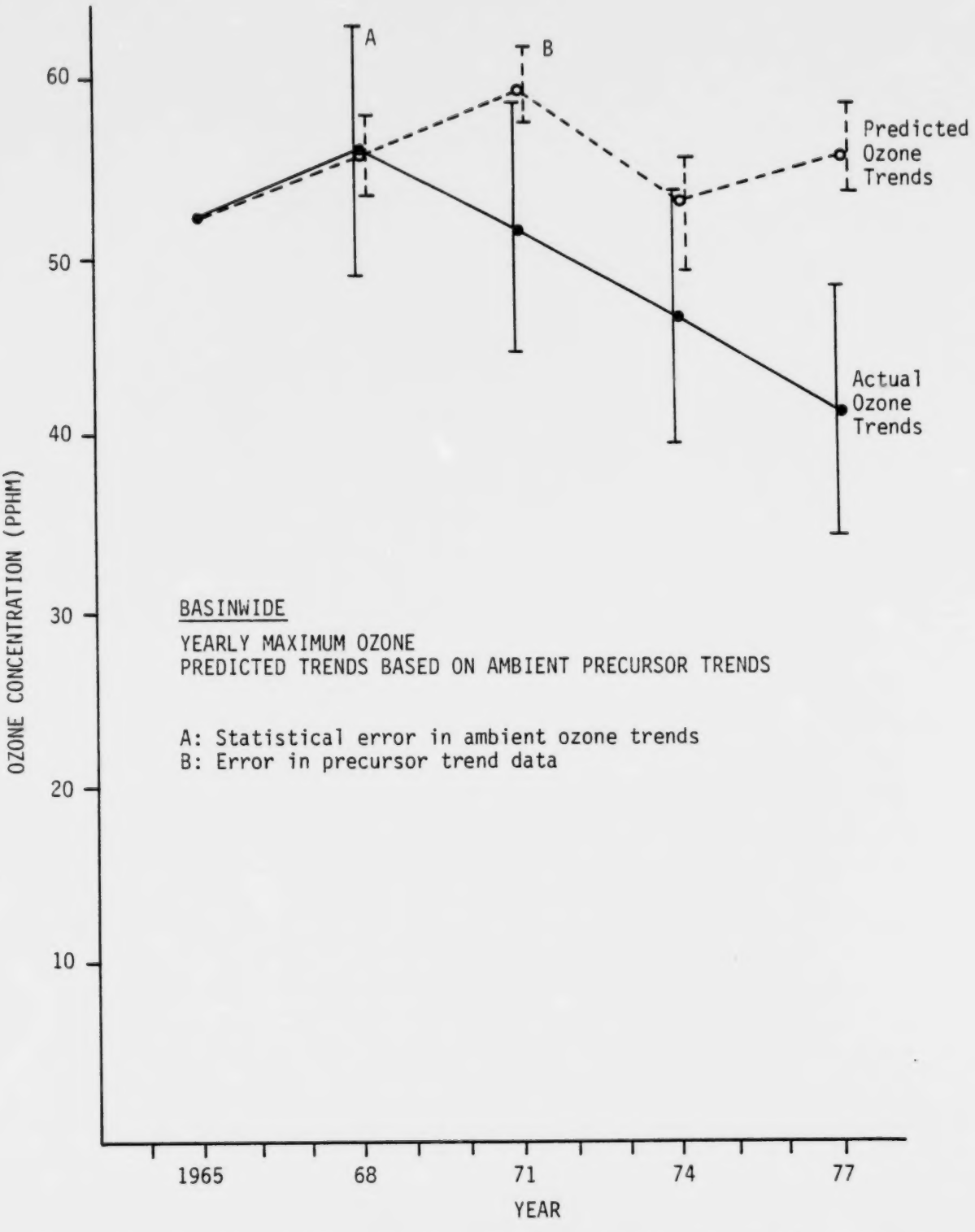

Figure 44. Results of the validation studies for basinwide yearly maximum ozone, using ambient precursor trends to derive predicted ozone trends.

DISCUSSION OF EKMA VALIDATION RESULTS

As indicated in the previous two sections, the EKMA model has not performed badly in predicting historical ozone trends within the Los Angeles region. There is, nevertheless, a cause for concern in the sense that the predicted ozone levels generally underestimate historical decreases in actual ozone levels, sometimes by a very substantial margin. The tendency for predicted ozone trends to underestimate historical ozone improvements was also observed in a previous EKMA validation study for Los Angeles (Trijonis and Hunsaker 1978). Actually, the discrepancies in the present study seem to be slightly less than those found in the previous study. Based on our sensitivity analyses (Chapter 4), we know that the major factor leading to better agreement in the present study is the addition of post 8 AM emissions to the EKMA simulations. The validation results in the present study would have improved even more if it were not for the fact that we used a higher NMHC/NO_x ratio than used in the previous study. The previous study used a ratio of 12:1; we changed this to a ratio of 13:1 after applying various corrections to the ambient NMHC and NO_x data.

It is important to investigate the cause of the observed discrepancies between predicted and actual ozone trends. Such an investigation might point to ways in which the application of EKMA can be improved. In the subsections which follow, we examine four major factors that could have produced the observed disagreements. These factors are (1) errors in the precursor trend data, (2) meteorological variance in actual ozone trends, (3) selection of specific EKMA simulation conditions, and (4) errors in the NMHC/NO_x ratio.

Errors in the Precursor Trend Data

One possible cause for the observed discrepancies between predicted and actual ozone trends could be errors in our estimates of historical precursor trends. These errors are represented by the (dashed line) error bars on the predicted ozone trends in Figures 27 through 44. After some thought, however, we conclude that errors in the precursor trends are <u>not</u> a significant factor leading to the disagreement. There are two reasons for this conclusion. First, the error bars representing the variance in historical precursor trends (see Figures 27 to 44) hardly seem large enough

to account for the major discrepancies. Second, and more important, the disagreement between predicted and actual ozone trends occurs whether we use emission data or ambient data to represent precursor trends. As discussed in Chapter 2, the agreement between emissions data and ambient precursor data gives us a rather high level of confidence in our historical precursor trends. The only way that errors in historical precursor trends could account for the observed discrepancy in ozone trends would be if two independent data sets (emissions data and ambient precursor data) each contained large, unexplainable errors in the same direction. This possibility seems highly unlikely.

Meteorological Variance in Actual Ozone Trends

The tendency for predicted ozone levels to underestimate historical decreases in actual ozone levels might possibly be explained by meteorological variance in the actual ozone trends. A priori, however, this does not seem very likely because the solid error bars in Figures 27 to 44 (representing the meteorological variance in ozone) are not nearly large enough to account for some of the discrepancies.

The issue of meteorological variance can be addressed more directly by examining ozone trends that have been normalized for meteorology. In a companion part of this project, Meisel et al. (1980) have derived met-adjusted ozone trends for Azusa. The air quality index they considered, smog-season/week-day average of daily maximal concentrations, differs from the two indices that we are using. This difference, however, may not be important because Trijonis (1980) has shown that ozone trends at Azusa and other Los Angeles sites are nearly identical for indices such as yearly maximum, 95th percentile of daily maxima, and yearly average of daily maxima.

The results of the analysis by Meisel et al. are summarized in Figure 45. This figure presents actual year-by-year ozone trends as well as met-adjusted ozone trends based on two weather normalization schemes (a 2-class scheme and a 5-class scheme). Already we can see that this met-adjustment analysis will not explain the discrepancies that we have observed between predicted and actual ozone trends. Firstly, the adjustments for meteorology are very small; secondly, the adjustments are in the wrong direction (met-adjusted ozone trends decrease even more rapidly than actual ozone trends

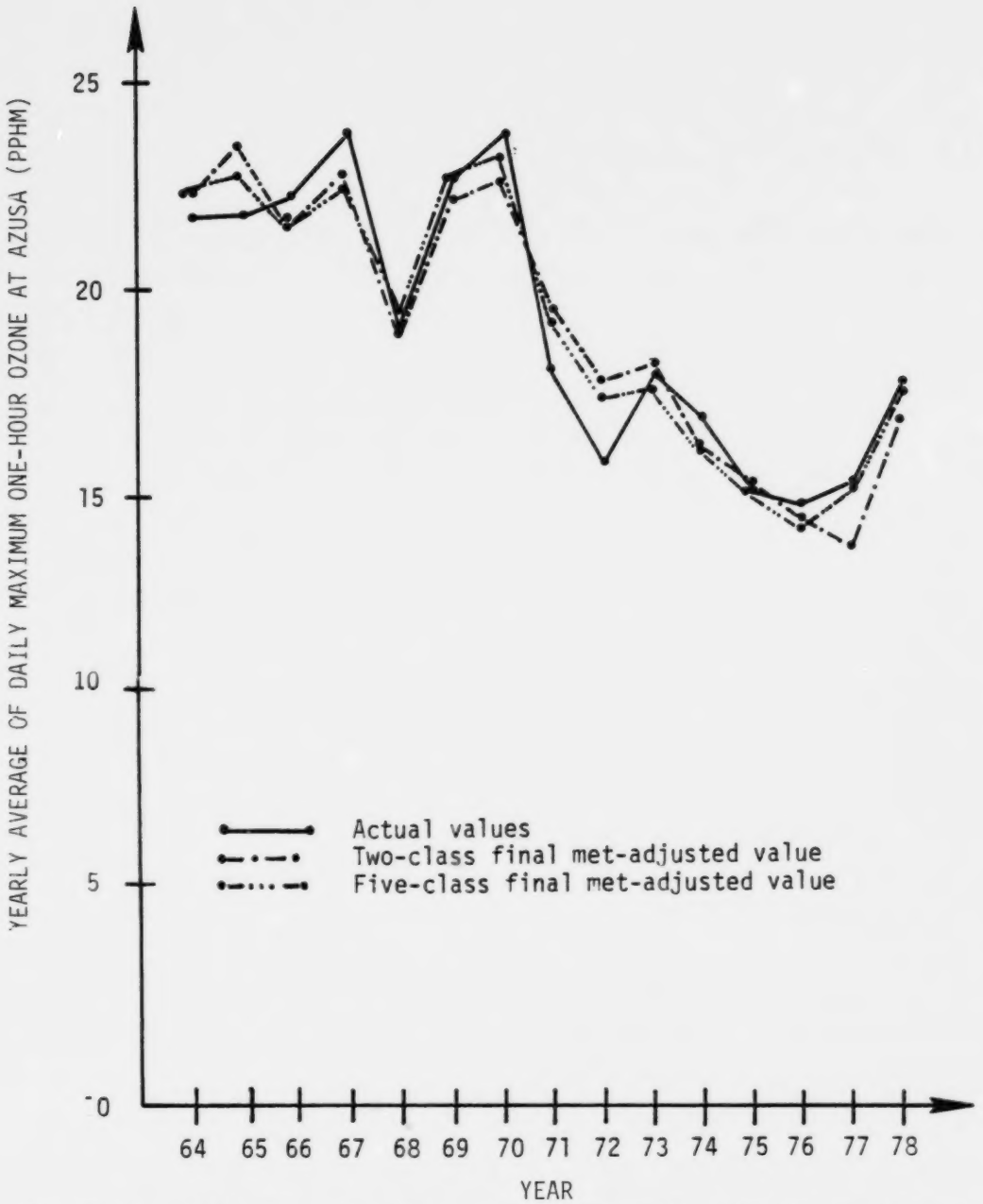

Figure 45. Comparison of actual ozone trends with met-adjusted trends based on two met-normalization schemes (Meisel et al. 1980).

because our base period, 1964-1966, had a low pollution potential for ozone). To make this result more explicit, we have normalized the results of Meisel et al. with respect to our base period and have plotted 3-year averages of the data (see Figure 46). It is obvious from Figure 46 that met-adjustment would make the discrepancy between predicted and actual trends worse by a very slight amount. Thus, it appears that meteorological variance in the actual ozone trends is not a major factor accounting for the discrepancy between predicted and actual ozone trends.

As a caveat to the above discussion, it should be noted that met-adjustment of air quality trends is an uncertain science. For one, generally accepted analytical procedures for met-adjustment have not been established. As a reflection of this problem, various studies have reached contradictory conclusions regarding met-adjusted ozone trends in Los Angeles (Cass 1980; Davidson 1980; Duckworth et al. 1980; Zeldin 1980). Furthermore, data may not even be available for certain meteorological phenomena that affect air quality trends.* Lacking such data we may not yet appreciate the significance of certain meteorological processes with respect to air quality trends. Also, as noted above, the analysis by Meisel et al. does not explicitly address the air quality indices that we have examined; our air quality indices may be subject to different types of meteorological influences than the index used by Meisel et al. Nevertheless, despite these caveats, the various studies conducted to date strongly suggest that meteorological variance is <u>not</u> the cause of the discrepancy that we have observed between predicted and actual ozone trends.

<u>Selection of Specific EKMA Simulation Conditions</u>

As discussed in Chapter 4, predicted ozone trends are moderately sensitive to the specific simulation conditions used to generate the EKMA isopleths. In fact, the discrepancy we find between predicted and actual ozone trends is less than that found by Trijonis and Hunsaker (1978) because we

*For example, we do not have meteorological data for Los Angeles that adequately reflect possible changes in residence time or carry-over pollution from previous days. Changes in residence time may have substantial impacts on precursor build-up and on subsequent ozone concentrations.

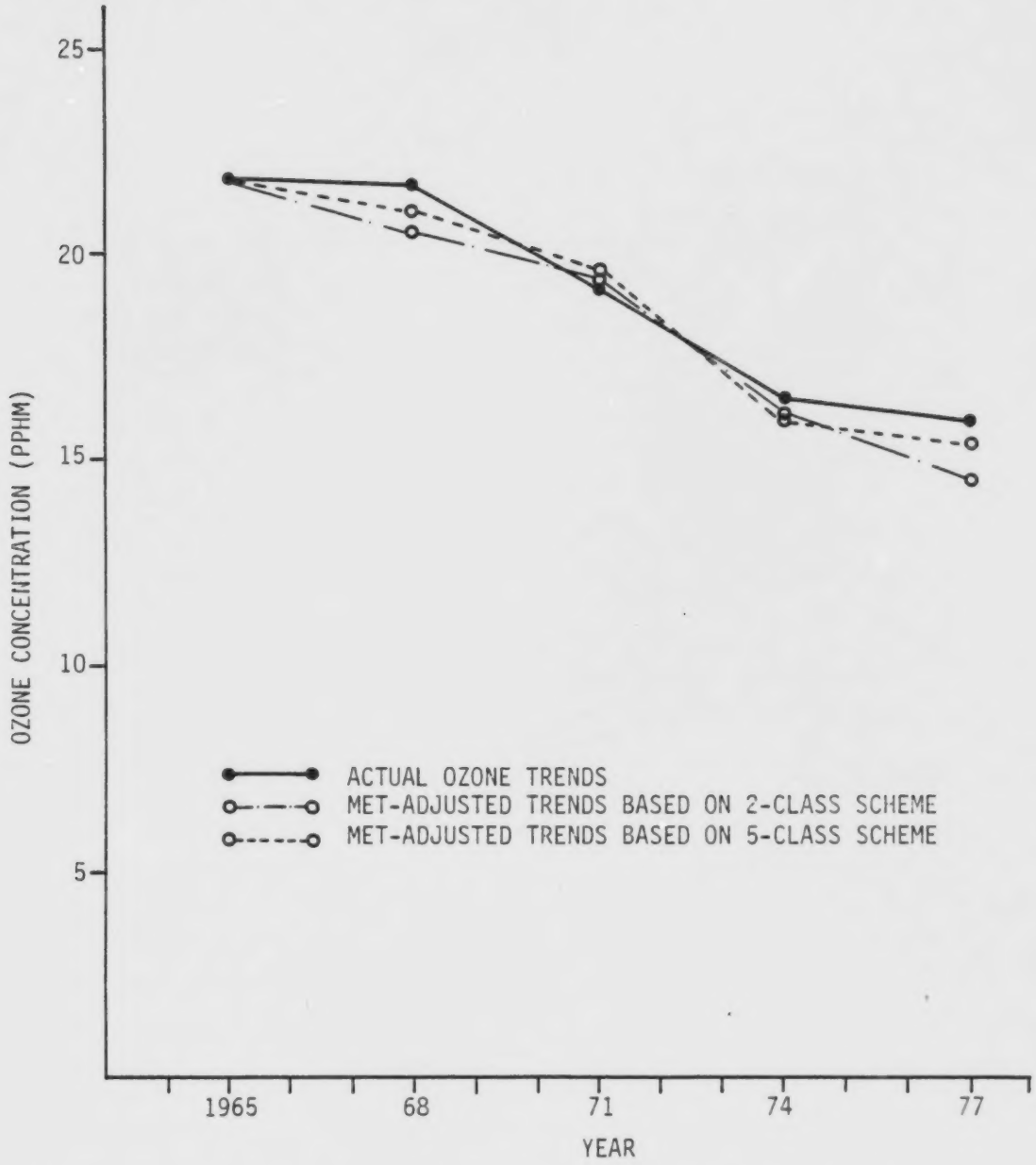

Figure 46. Met-adjusted ozone trends at Azusa normalized to conditions in the base period (1964-1966).

have used EKMA isopleths based on simulations including post 8 AM emissions. Perhaps, the discrepancy would be reduced even more by further refinements of the EKMA simulation conditions.

Two potential refinements in the EKMA simulation conditions immediately come to mind. The first is to include some degree of background or carry-over ozone in the simulations. The isopleths that we have used assume that dilution takes place with ozone-free air as the mixing height rises during the day. It would be more realistic to assume a significant background ozone level in the dilution air (either a natural background of $\sim$ .03 to .05 ppm or a carry-over, man-made background of .10 to .20 ppm). The second refinement concerns our estimate of the overall dilution rate. The mixing height change that we have used, 150 meters at 8 AM to 600 meters at 5 PM, may not best represent mixing height changes on high ozone days in Los Angeles. A study of the mixing height change experienced by air parcels as they traverse the Los Angeles basin would have to be performed in order to determine the most appropriate dilution rate.

Although the discrepancy between predicted and actual ozone trends might be reduced somewhat by refining the EKMA simulation conditions, we doubt that such refinements would erradicate the discrepancy. As shown previously in Figures 18 to 21 (pages 56 to 59), predicted ozone trends are only moderately sensitive to the EKMA simulation conditions. Furthermore, the simulation conditions that we have used already yield nearly the best agreement (between predicted and actual trends) among the six EKMA simulation conditions considered. Also, we have done some preliminary tests with EKMA isopleths that do include background ozone and have found that these isopleths do not improve our results. Because of these reasons, we doubt that further refinements of the EKMA simulation conditions will have enough leverage to eliminate all (or even most) of the discrepancy.

Error in the NMHC/NO_X Ratio

The single obvious factor that does have the leverage to account for the observed discrepancy is error in the NMHC/NO_X ratio. As discussed in Chapter 4, predicted ozone trends are very sensitive to the NMHC/NO_X ratio,

so that potential errors in the ratio could easily account for any discrepancies between predicted and actual ozone trends.

Figures 47 through 51 compare actual ozone trends to predicted ozone trends, with the latter based on a 10:1 NMHC/NO_x ratio rather than a 13:1 ratio. These figures include predictions based on both emission trends and ambient precursor trends. To make the results more compact, we have included yearly maximum ozone and 95th percentile of daily maximum ozone in the same figures.

Figures 47 to 51 show that using a ratio of 10:1 nearly eliminates the general tendency for predicted ozone trends to underestimate historical decreases in actual ozone trends. Although we have not included error bars in these figures, it is obvious from the size of our previous error bars (Figures 27 to 44) that essentially all of the predicted and actual trends would now agree within the errors imposed by variance in precursor trends and meteorological fluctuations in actual ozone trends. Thus, we conclude that a 23% decrease in the NMHC/NO_x ratio (from 13:1 to 10:1) would nearly eliminate the basic discrepancy.

It should be noted that there are two ways in which the NMHC/NO_x ratio could be in error. First, we could be dealing with <u>random</u> error in our estimate of the ratio -- an error that would not necessarily reproduce itself in applying EKMA to other areas. As discussed in Chapter 4, there are significant disagreements among some of the data bases we examined regarding the NMHC/NO_x ratio. Although we thought that most of the data supported a value of 13:1, this value could be off due to undocumented instrument errors in some of the monitoring programs or due to meteorological variance in the ratio during the monitoring periods.

The second type of error in the NMHC/NO_x ratio could be a systematic error in matching the atmospheric NMHC/NO_x ratio with the EKMA NMHC/NO_x ratio. In Chapter 4, we attempted to eliminate this type of systematic error by making two adjustments to the ambient NMHC/NO_x ratio: (1) adjusting ambient NMHC data based on methane calibrated instruments upward by a factor of 1.43 to make the data approximately equivalent to measurements made with propane calibrated instruments (i.e. to make the

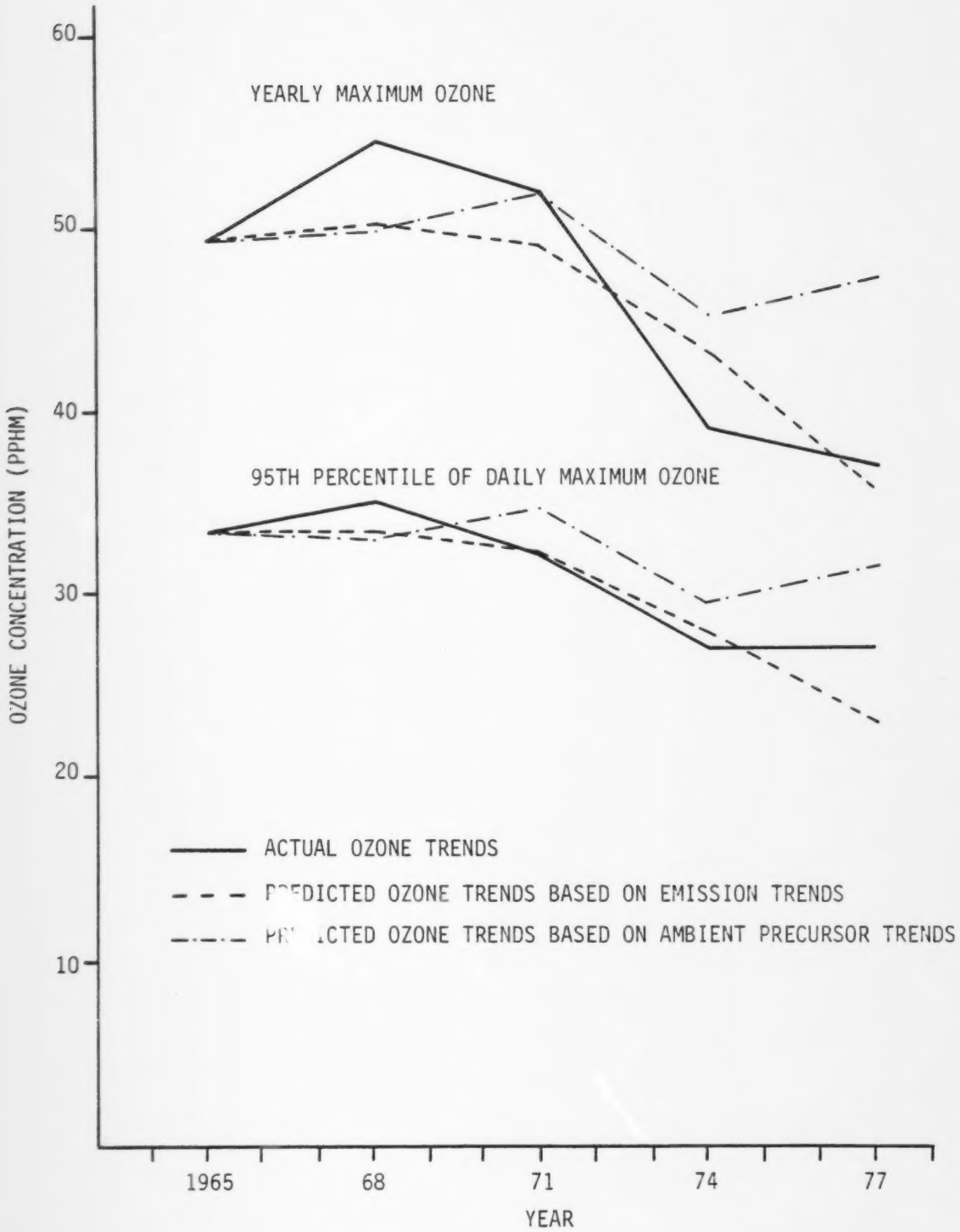

Figure 47. Results of validation studies at Azusa using an NMHC/NO_x ratio of 10:1.

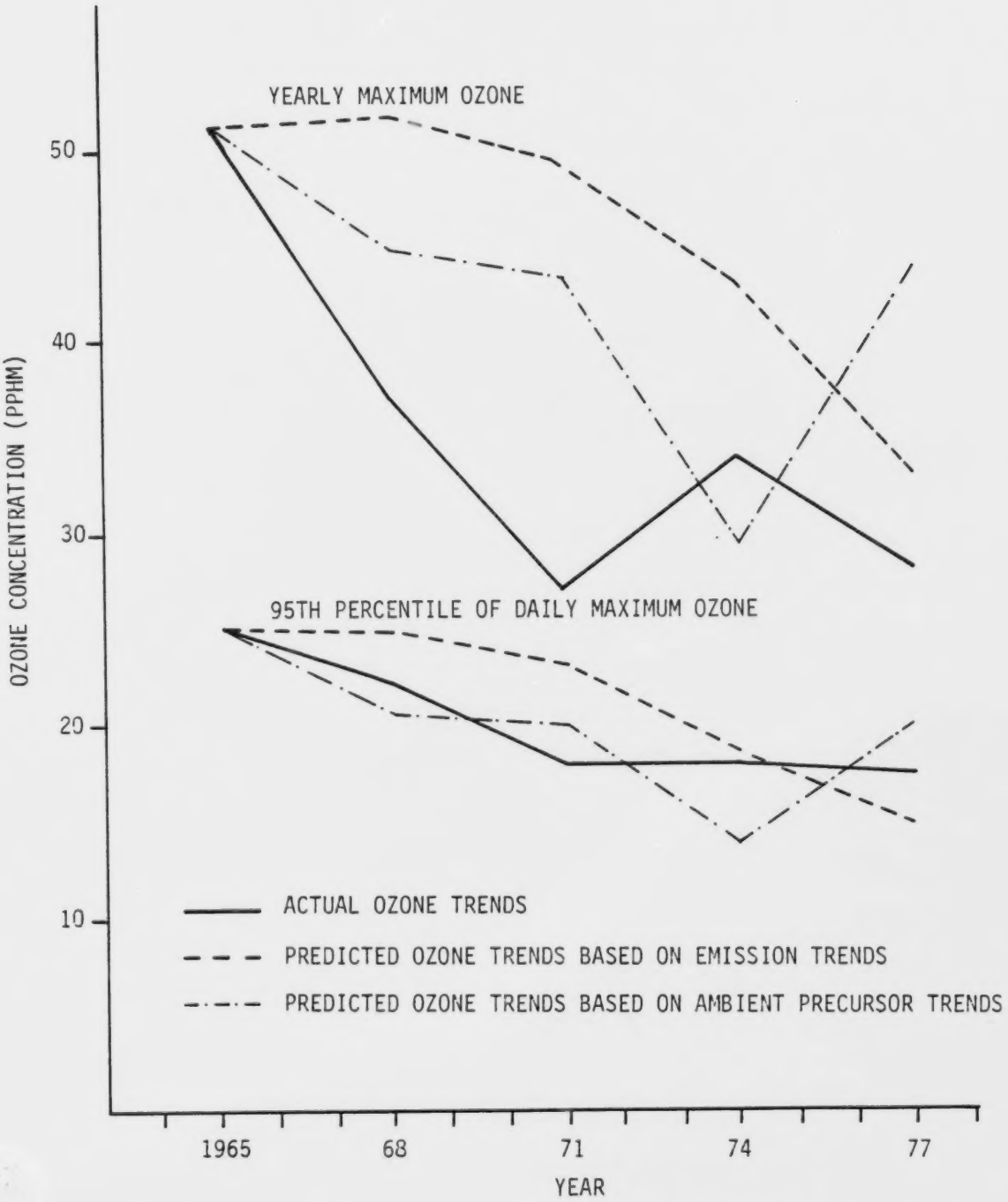

Figure 48. Results of validation studies at Downtown Los Angeles using an $NMHC/NO_x$ ratio of 10:1.

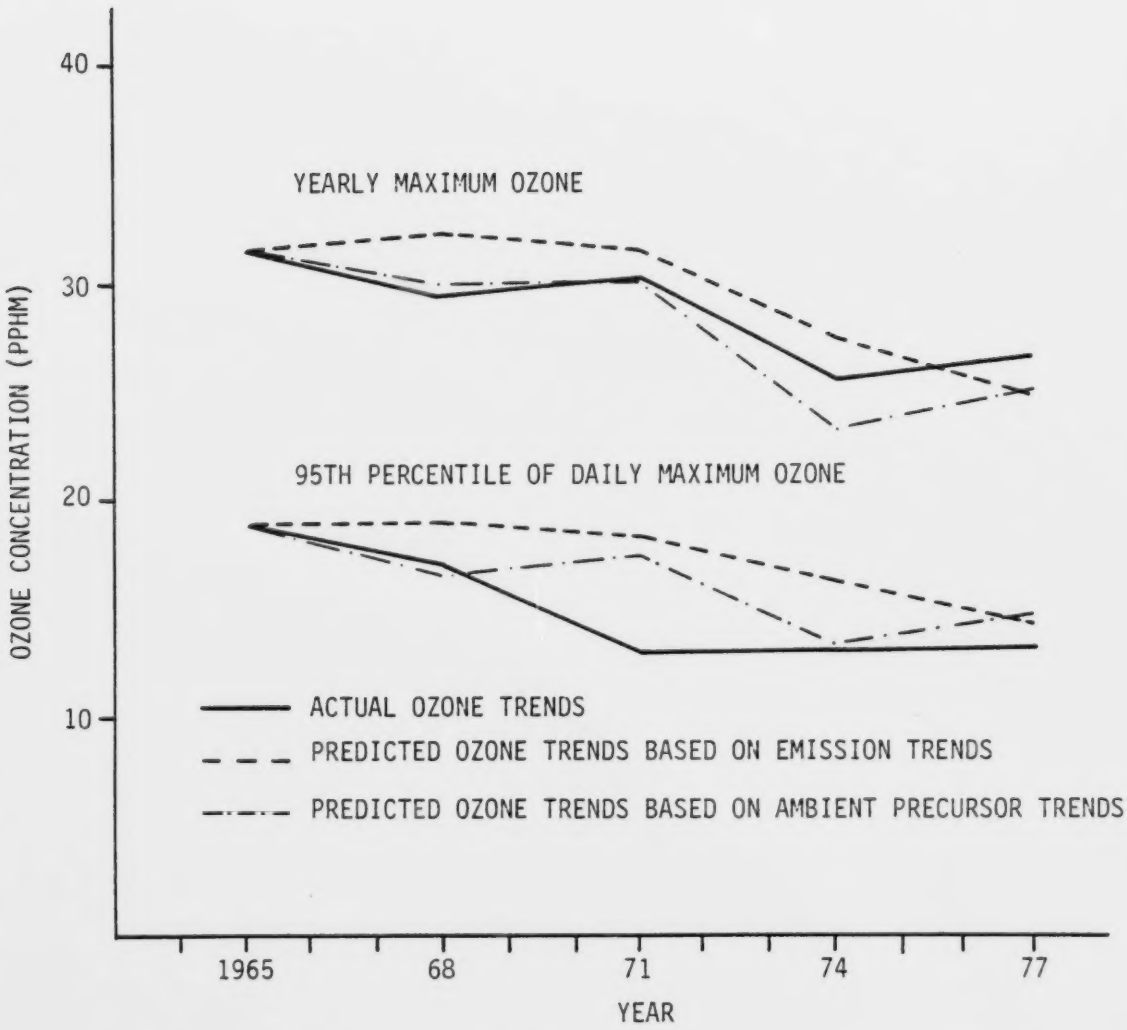

Figure 49. Results of validation studies at Anaheim using an NMHC/NO_x ratio of 10:1.

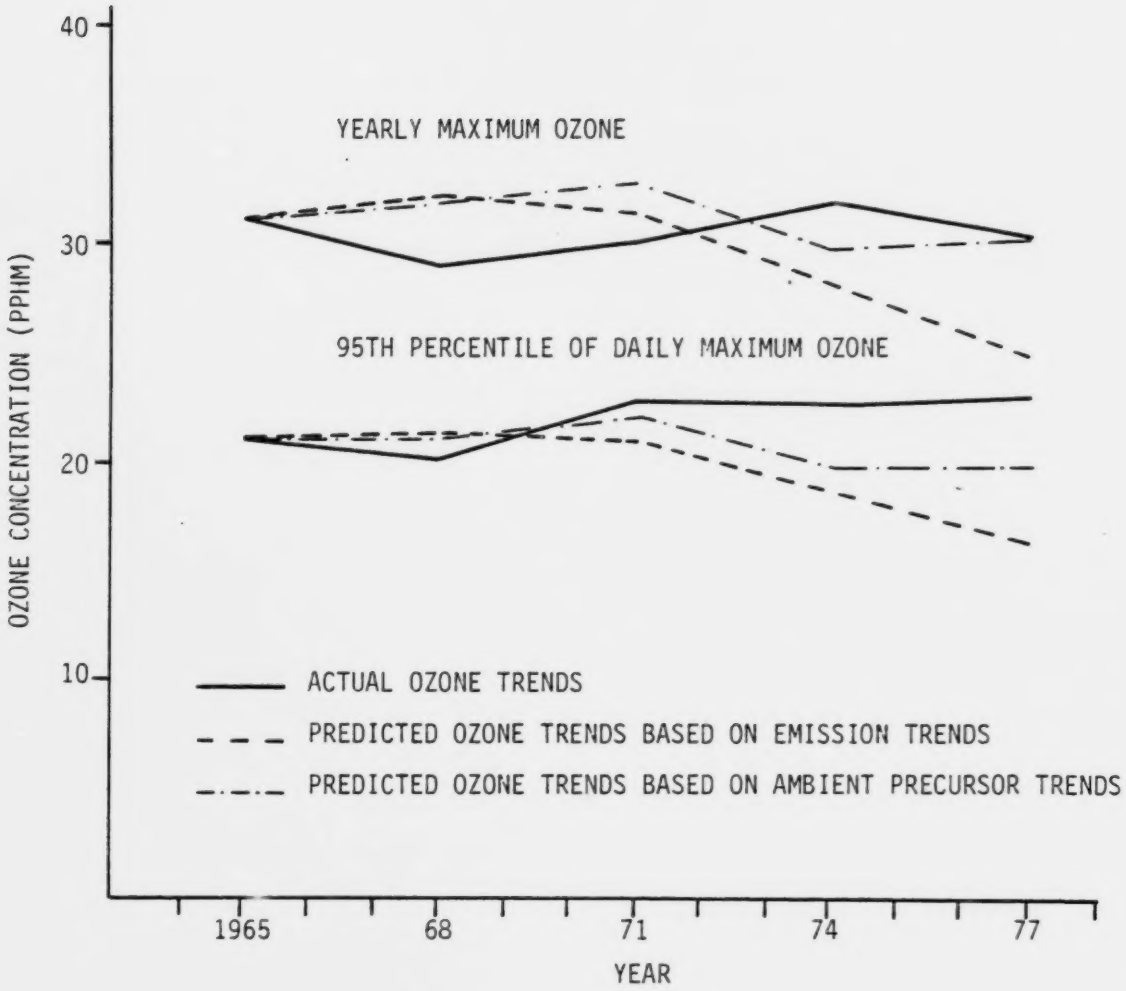

Figure 50. Results of validation studies at San Bernardino using an $NMHC/NO_x$ ratio of 10:1.

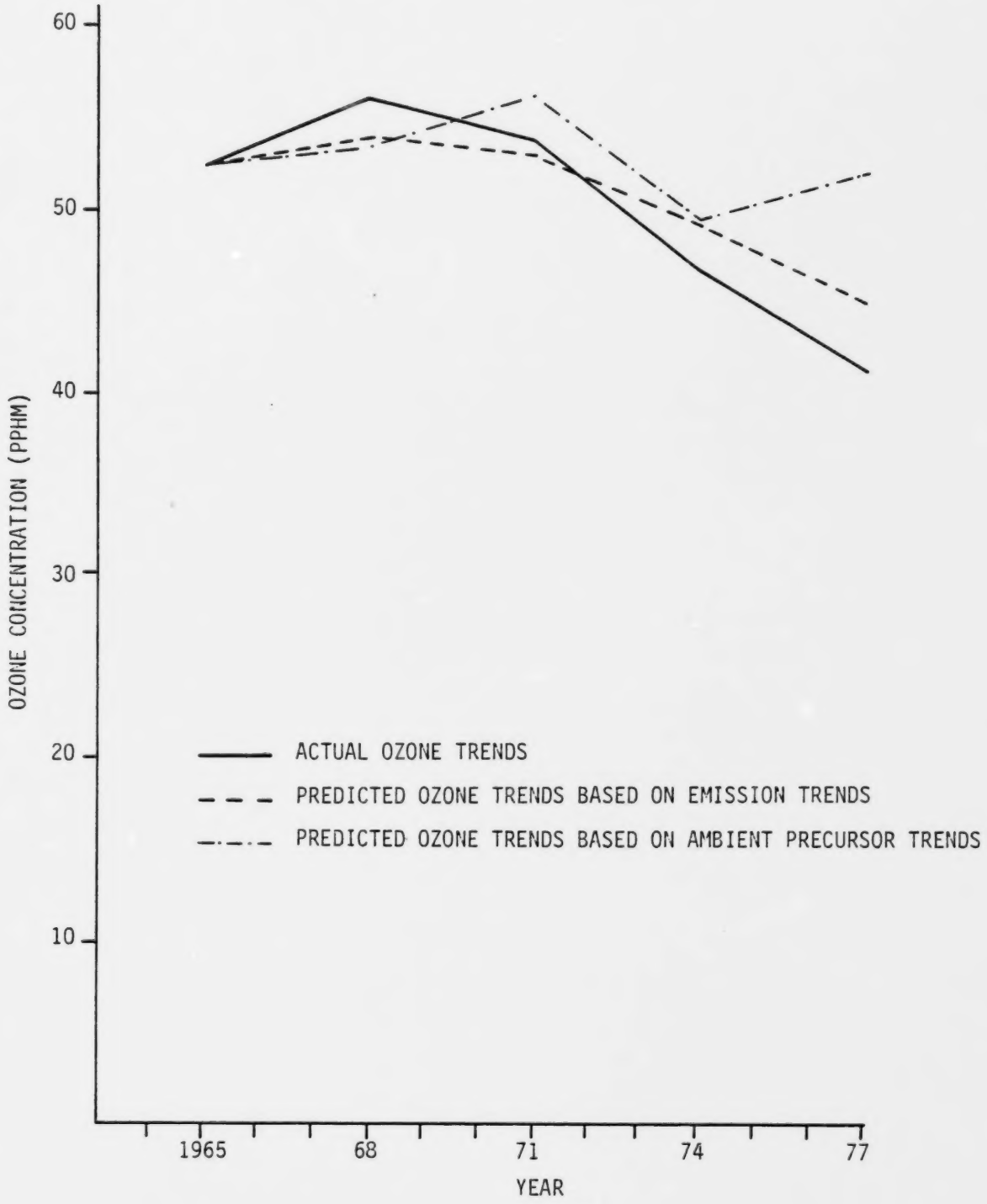

Figure 51. Results of validation studies for basinwide maximum ozone using NMHC/NO_x ratio of 10:1.

ambient NMHC measurement technique approximately equivalent to the technique used in the chamber studies that serve as a foundation for EKMA) and (2) adjusting the NMHC/NO_x ratio downward by a factor of 0.9 to account for the fact that Los Angeles atmospheric NMHC contains about 10% of the nearly nonreactive compounds ethane and propane, while the chamber studies on which EKMA is based contain essentially no ethane and propane. Ironically, the net effect of these adjustments was to increase the ambient NMHC/NO_x ratio by a factor of 1.3 (1.43 x .90). That is, if we had not made the adjustments we would have had a significantly lower ratio and would not have observed the discrepancy between predicted and actual ozone trends.

There may, however, be other systematic differences between atmospheric NMHC/NO_x ratios and EKMA NMHC/NO_x ratios that we have not accounted for. For example, even though we adjusted for the extra ethane and propane in atmospheric NMHC, the remaining ambient NMHC may still be less reactive than EKMA NMHC. Also, there may be a basic difference between EKMA simulation conditions and atmospheric conditions that leads to a displacement of the critical NMHC/NO_x ratio (i.e. the ratio that defines the crest of the ozone "hill" in the ozone isopleth diagram). In this regard, we note that Carter et al. (1981) have found that EKMA predictions are sensitive to the chemical-kinetic mechanism used in EKMA. In fact, Carter et al. conclude that improving the chemical-kinetic mechanism in EKMA would make predicted ozone significantly more sensitive to NMHC control. If this conclusion is valid, it is directly relevant to our study because the effect would be in the right direction to reduce the discrepancies that we have observed. We cannot say that a systematic discrepancy exists between the atmospheric NMHC/NO_x ratio and the EKMA NMHC/NO_x ratio and/or between atmospheric chemistry and EKMA kinetic mechanisms, but neither can we rule out the possibility of such a discrepancy. Further thought should be given regarding ways to check the equivalency between the atmospheric and EKMA NMHC/NO_x ratios as well as between atmospheric and EKMA chemical mechanisms.

Implications Regarding the Application of EKMA

The results of this study apparently point to two significant implications regarding the future application of EKMA in predicting ozone changes produced by NMHC and NO_x emission changes. The first is that the predictions can be moderately sensitive to the specific EKMA simulation conditions (e.g. dilution rate or inclusion of post 8 AM emissions). Thus, it may be important, in some applications, to insure that the most realistic, area-specific EKMA simulation conditions are used.

The second, more important implication is that the EKMA predictions can be very sensitive to the NMHC/NO_x ratio. This implies that care should be taken in each application to obtain an accurate estimate of the NMHC/NO_x ratio. Furthermore, research should be conducted to test the validity of the chemical-kinetic mechanism in EKMA and to check that atmospheric NMHC/NO_x ratios are indeed equivalent to EKMA NMHC/NO_x ratios. This research might lead to improved chemical mechanisms for EKMA or to guidelines for adjusting atmospheric NMHC/NO_x ratios before they are used in EKMA.

It should be noted that the above implications regarding the application of EKMA are most important in situations where NMHC emissions are being reduced and NO_x emissions are being increased* (such as occurred historically in Los Angeles). In such situations, the predictions of EKMA are especially sensitive to the specific simulation conditions and the NMHC/NO_x ratio. The implications would not be that important if NMHC and NO_x emissions were undergoing similar changes (i.e. both increasing or both decreasing). When NMHC and NO_x undergo like changes, the predictions of EKMA are not very sensitive to the simulation conditions or to the NMHC/NO_x ratio (Davis and Trijonis 1981). Because of the federal motor vehicle control program, NMHC and NO_x emissions in many urban areas will both be decreasing in the future; fortunately, this implies that the selection of EKMA simulation conditions and NMHC/NO_x ratios may not be that critical in predicting future ozone levels.

*More generally, the implications are important when NMHC emissions and NO_x emissions are undergoing dissimilar changes.

A NOTE ON RECENT LOS ANGELES OZONE TRENDS

As a postscript to this study, it is worthwhile to briefly discuss the controversy surrounding recent ozone trends in the Los Angeles area. The controversy concerns the fact that, although ozone levels decreased substantially at most sites in Los Angeles from the middle 1960s to the middle 1970s, there has been a lack of improvement since the middle 1970s. The recent lack of improvement in ozone was the subject of a symposium at Caltech in January 1980. At that symposium, several possible explanations were considered:

- Growth. Growth in sources (e.g. traffic) may have outstripped the effects of controls.
- Catalytic Converters. Hydrocarbon emissions from automobiles may not be decreasing due to poisoned or defective catalytic converters.
- Meteorology. Meteorological pollution potential for ozone may have been higher during recent years.
- NMHC/NO_x Ratio. Reducing ozone in Los Angeles may essentially depend on reducing the NMHC/NO_x ratio; the historical tendency of a decreasing NMHC/NO_x ratio apparently stopped in the middle 1970s.
- Failure of Control Programs. The overall control programs for NMHC and NO_x in Los Angeles may be failing due to deterioration in existing mobile and stationary source control devices, underestimation of growth in certain source categories, or misestimation of the relative amount of emissions from controlled versus uncontrolled source categories.

The Caltech symposium was not able to reach a conclusion as to the real cause of the recent lack of improvement in ozone. In fact, the cause still is unknown (Holmes 1981).

Although the present study cannot resolve the controversy concerning recent ozone trends in Los Angeles, it does provide some further insights. For example, this study suggests that growth in traffic has not outstripped

the automotive controls. In compiling emission trends (Chapter 2), we included the effects of traffic growth but still found that hydrocarbon emissions were decreasing during the late 1970s at least as rapidly as they had declined during the late 1960s and early 1970s. Likewise, this study suggests that the cause is not failure of the catalyst control program. Our emission trend data includes the effect of mis-fueled or defective catalysts; despite this effect, we find that hydrocarbon emissions continued to decrease in the late 1970s at the same rate as earlier years. The only way that traffic growth or catalyst failures could account for the lack of ozone improvement would be if our data bases on traffic and defective catalysts were in error. Although these data bases should be checked and updated, we think it is unlikely that they contain substantial errors.

Researchers at the Caltech symposium indicated that meteorology is probably not the cause of the recent lack of ozone improvement. The various met-adjustment schemes applied by Cass (1980), Davidson (1980), Duckworth et al. (1980), and Zeldin (1980) all showed that, even when adjusted for meteorology, ozone levels did not decrease in the late 1970s (some researchers in fact found that met-adjusted ozone trends increased during the late 1970s). However, as discussed previously in this chapter, the existing met-adjustment methodologies are subject to significant uncertainties. The results of the present study suggest that meteorology may actually be partly responsible for the recent lack of ozone improvement. As discussed in Chapter 2, we found that, from 1973-1975 to 1976-1978, ambient NMHC increased (approximately 5-10%) despite a 10% decrease in estimated RHC emissions, and ambient NO_x increased (approximately 5-10%) despite nearly constant NO_x emissions. This suggests that dispersive conditions for the precursors may have been lower in 1976-1978 than in 1973-1975. Considering the nature of the met-adjustment techniques employed for Los Angeles ozone by various researchers, it is quite possible that these techniques failed to account for a decrease in dispersive conditions with respect to ozone precursors (such as might result from increased residence times for air parcels in the basin). Thus, meteorology may indeed be responsible for

the recent lack of ozone improvement despite the contrary conclusion of existing met-adjustment studies.

If meteorology (or monitoring errors for NMHC and NO_x) is not responsible for the upturn in ambient precursor concentrations from 1973-1975 to 1976-1978, then we must fall back on the last of the potential explanations listed above -- overall failure of control programs. That is -- if ambient precursor levels are really increasing despite projected decreases in emissions, then there is a failure in the overall control programs that are supposedly producing those emission decreases.

Lastly, we note that the explanation involving changes in the $NMHC/NO_x$ ratio make sense to a degree. Ozone concentrations in Los Angeles stopped their historical decrease in approximately 1974; this is the time when NO_x controls started to have a significant effect (see Figure 2 page 13); this is also the time when the ambient $NMHC/NO_x$ ratio stopped its historical decrease (see Figure 17 page 52). The explanation involving the $NMHC/NO_x$ ratio, however, does not account for observation that ambient precursor levels increased in the late 1970s relative to the middle 1970s.

All considered, the recent lack of improvement in ozone within the Los Angeles region is still a mystery. There are several potential explanations, each of which seems reasonable to a degree, but each of which seems to contradict certain data. It appears that new data must be taken and more analyses must be conducted before the issue can be resolved.

REFERENCES

ARB (Air Resources Board), "Ten-Year Summary of California Air Quality Data, 1963-1972," State of California Air Resources Board, Air Analysis Section, Sacramento, California, January 1974.

ARB (Air Resources Board), "California Air Quality Data, Quarterly Summaries," State of California Air Resources Board, Technical Services Division, Sacramento, California, 1976-1978.

ARB (Air Resources Board), "Three-Year Summary of California Air Quality Data, 1973-1975," State of California Air Resources Board, Technical Services Division, Sacramento, California, January 1977.

ARB (Air Resources Board), "Procedure and Basis for Estimating On-Road Motor Vehicle Emissions," State of California Air Resources Board, Technical Services Division, Sacramento, California, January 1980a.

ARB (Air Resources Board), "1976 Emissions Inventory for California," Personal Communication of Data from Technical Services Division of State of California Air Resources Board, Sacramento, California, 1980b.

Bartz, D.R. et al., "Control of Oxides of Nitrogen from Stationary Sources in the South Coast Air Basin", Prepared at KVB, Tustin, California, for Air Resources Board, State of California, KVB Report No. 5800-179, ARB Contract 2-1471, September 1974.

Carter, W., A. Winer, and J. Pitts, "Effects of Kinetic Mechanisms and Hydrocarbon Composition on Oxidant-Precursor Relationships Predicted by the EKMA Isopleth Technique," Atmospheric Environment, paper by the Statewide Air Pollution Research Center, Riverside, California, to appear in early 1981.

Cass, G., "Meteorological and Chemical Potential for Oxidant Formation," Presented at the Conference on Air Quality Trends in the South Coast Air Basin, Pasadena, California, February 21, 1980.

Davidson, A., "Air Quality Trends in the South Coast Air Basin - Presentation II," Presented at the Conference on Air Quality Trends in the South Coast Air Basin, Pasadena, California, February 21, 1980.

Davis, M. and J. Trijonis, "Historical Emission and Ozone Trends in the Houston Area," Prepared at Santa Fe Research Corporation under subcontract to Technology Service Corporation, For U. S. Environmental Protection Agency (Contract #68-02-2976), February 1981.

Dimitriades, B., "On the Function of Hydrocarbon and Nitrogen Oxides in Photochemical Smog Formation," U.S. Bureau of Mines Report of Investigations RI 7433, September 1970.

Dimitriades, B., "Effects of Hydrocarbon and Nitrogen Oxides on Photochemical Smog Formation," Eviron. Sci. Technol., Volume 6, 1972.

Dimitriades, B., "The Concept of Reactivity and Its Possible Applications in Control," Proceedings of the Solvent Reactivity Conference, EPA-650/3-74-010, November 1974.

Dimitriades, B., "An Alternative to the Appendix J Method for Calculating Oxidant-and-NO_2-Related Control Requirements," EPA-600/3-77-001b, 1977a.

Dimitriades, B., "Oxidant Control Strategies, Part 1, Urban Oxidant Control Strategy Derived from Existing Smog Chamber Data," Environ. Sci. Technol., Volume 11, 1977b.

Duckworth, S. et al., "Analysis of Meteorological and Other Factors Influencing Air Quality Trends," Presented at the Conference on Air Quality Trends in the South Coast Air Basin, Pasadena, California, Feb. 21, 1980.

Eldon, J. and J. Trijonis, "Statistical Oxidant Precursor Relationships for the Los Angeles Region, Part I. Data Quality Review and Evaluation," Interim Report to the Air Resources Board under Contract No. A5-020-87, January 1977.

EPA (Environmental Protection Agency), "Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors," EPA-450/2-77-021a, U.S. EPA, Research Triangle Park, North Carolina, November 1977.

EPA (Environmental Protection Agency), "Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors: Supporting Documentation," EPA-450/2-77-021b, U.S. EPA, Research Triangle Park, North Carolina, February 1978a.

EPA (Environmental Protection Agency), "Mobile Source Emission Factors," National Technical Information Service, PB-295 672, Springfield, Virginia, March 1978b.

EPA (Environmental Protection Agency), "Guidelines for Use of City-specific EKMA in Preparing Ozone SIPs (Draft)," EPA-450/4-80-027, U.S. EPA, Research Triangle Park, North Carolina, October 1980.

Holmes, J., California Air Resources Board, Sacramento, California, Personal Communication, 1981.

Horie, Y. et al., "Ozone Precursor Emissions/Air Quality Relationships For Use with the Empirical Kinetic Modeling Approach," Prepared at Technology Service Corporation (TSC-PD-A196-6), Santa Monica, California, for U.S. Environmental Protection Agency (Contract No. 68-02-2891), Research Triangle Park, North Carolina, July 1979.

Kinosian, J., "Confirmation of Ozone Trends," Presented at the Conference on Air Quality Trends in the South Coast Air Basin, Pasadena, California February 21-22, 1980.

LARTS (Los Angeles Regional Transportation Study), "LARTS Base Year Report, 1967 Origin-Destination Survey," Los Angeles Regional Transportation Study, Los Angeles, California, December 1971.

LARTS (Los Angeles Regional Transportation Study), "The 1976 Urban and Rural Travel Survey, Volume IV, Summary of Findings: Travel Data," Los Angeles Regional Transportation Study, Los Angeles, California, October 1979.

LARTS (Los Angeles Regional Transportation Study), Los Angeles, California, Personal Communication of Data from Charles Bare, 1980.

Meisel, Wm. et al., "The Impact of Meteorology on Oxidant Air Quality Trends in Los Angeles," Prepared at Technology Service Corporation (TSC-PD-A213-7), Santa Monica, California, for U.S. EPA (Contract No. 68-02-2976), Research Triangle Park, North Carolina, January 1980.

Meyer, Edwin, U.S. EPA, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, Personal Communication, 1980.

Paskind, J. and J. Kinosian, "Hydrocarbon, Oxides of Nitrogen and Oxidant Pollutant Relationships in the Atmosphere Over California Cities," Presented at the 67th Annual Meeting of the Air Pollution Control Association, Denver, Colorado, June 9-13, 1974.

Platte, Lois, U.S. EPA, Office of Mobile Source Air Pollution Control, Ann Arbor, Michigan, Personal Communication, 1980.

SCAG (Southern California Association of Governments), "First Annual Reasonable Further Progress Report on the South Coast Air Quality Management Plan," Southern California Association of Governments and South Coast Air Quality Management District, Los Angeles, California, July 1, 1980.

SCE (Southern California Edison), "Power Plant NO_x Emissions and Ambient Air Quality in the South Coast Air Basin," Prepared by Research and Development Department of Southern California Edison Company, January 23, 1980.

Schere, K. and K. Demerjian, "A Photochemical Box Model Urban Air Quality Simulation," Proceedings of the Fourth Joint Conference on the Sensing of Environmental Pollutants, American Chemical Society, 1978.

Taback H. et al., "Control of Hydrocarbon Emissions from Stationary Sources in the California South Coast Air Basin," Prepared at KVB (KVB 5804-714), Tustin, California, for California Air Resources Board (ARB 5-1323), Sacramento California, June 1978.

Trijonis, J., "Oxidant and Precursor Trends in the Metropolitan Los Angeles Region: An Update," Report to California Air Resources Board under Contract No. A9-095-31, February 1980.

Trijonis, J. and K. Arledge, "Utility of Reactivity Criteria in Organic Emission Control Strategies, Application to the Los Angeles Atmosphere," EPA-600/3-76-091, U.S. EPA, Research Triangle Park, NC, August 1976.

Trijonis J. and D. Hunsaker, "Verification of the Isopleth Method for Relating Photochemical Oxidant to Precursors," EPA-600/3-78-019, U.S. EPA, Research Triangle Park, NC, February 1978.

Trijonis, J. et al., "An Implementation Plan for Suspended Particulate Matter in the Los Angeles Region," Prepared at TRW Inc., under Contract No. 68-02-1384 to the U.S. EPA, March 1975.

Trijonis, J. et al., "Oxidant and Precursor Trends in the Metropolitan Los Angeles Region," Atmospheric Environment, Volume 12, 1978.

Wallis, J., U.S. EPA, Office of Mobile Source Air Pollution Control, Ann Arbor, Michigan, Personal Communication, 1980.

Zeldin, M., Meteorological Consultant, San Bernardino, California, Personal Communication, 1978.

Zeldin, M., "Can Short-Term Air Quality Forecast Procedures Be Used in Retrospect to Normalize Air Quality Trends to Conditions of Constant Meteorology?," Presented at the Conference on Air Quality Trends in the South Coast Air Basin, Pasadena, Caliofrnia, February 21, 1980.

APPENDIX A

DESCRIPTION OF EMISSION TREND CALCULATIONS

This appendix describes the data, assumptions, and methods used to derive emission trend estimates for hydrocarbons and nitrogen oxides. The discussion is organized according to stationary sources of hydrocarbons, stationary sources of NO_x, and mobile sources of hydrocarbons and NO_x.

STATIONARY HYDROCARBON SOURCES

A recent, comprehensive inventory of hydrocarbon emissions from stationary sources in Los Angeles compiled by Taback et al. (1978) is used as the base year inventory for stationary sources of reactive hydrocarbons (RHC). This inventory pertains to the year 1976; it is projected backward and forward in time according to the methods discussed in the subsections below.

It should be noted that the hydrocarbon emission trends compiled herein refer to reactive hydrocarbons (RHC). Estimates of RHC emissions are derived from data on total hydrocarbon emissions using a two-group reactivity classification scheme proposed by Dimitriades (1974), with reactivity ratings specific to Los Angeles source categories calculated by Trijonis and Arledge (1976).

Table A-1 summarizes emission trends for the four major categories of stationary RHC sources: organic solvents, petroleum refining/production, petroleum marketing, and other stationary sources. The methods used to derive emissions for each of these categories are described below.

Organic Solvents

Although the organic solvent category contains several distinct types of sources, trends are estimated in aggregate for this category during the period 1965 to 1974 because it is difficult to obtain trend information for individual source types before 1974. We have assumed that total RHC emissions from organic solvents decreased 20% from 1965 to 1970 as a result of SCAQMD* Rule 66 (APCD 1971; Trijonis et al. 1976; Weiss 1980). This

*South Coast Air Quality Management District.

TABLE A-1. SUMMARY OF EMISSION TRENDS FROM STATIONARY SOURCES OF RHC.

YEAR	RHC EMISSIONS BY SOURCE CATEGORY (TONS/DAY)				
	Organic Solvents	Petroleum Refining/Production	Petroleum Marketing	Other Stationary Sources	Total
1965	280	102	104	25	511
1966	269	102	108	25	504
1967	258	102	110	26	496
1968	247	102	115	26	490
1969	235	102	120	27	484
1970	224	102	124	28	478
1971	213	102	127	28	470
1972	202	102	134	29	467
1973	191	102	137	29	459
1974	180	102	131	30	443
1975	179	102	134	31	446
1976	183	102	114	31	430
1977	180	102	97	32	411
1978	178	93	102	33	406

reduction from 1965 to 1970 represents not only controls on total hydrocarbon emissions but also substitution controls that reduced hydrocarbon reactivity. We have also assumed a 20% reduction of organic solvent RHC emissions from 1970 to 1974 due to continued organic solvent control programs instituted by the SCAQMD (Trijonis et al. 1976; Weiss 1980).

For the period 1974 to 1978 we consider trends individually for various types of organic solvent sources: non-architectural surface coatings, architectural surface coatings, domestic solvent use, drycleaning, degreasing, printing, and miscellaneous solvent use. Our methodologies for estimating trends for each of these source types are described in the paragraphs that follow.

Non-architectural surface coating, the single largest source type in the organic solvent category, includes automobile priming/topcoating and paper treatment. Some substitution of water-base coatings for petroleum-base coatings was included in the organic solvent controls instituted by 1974. RHC emissions are assumed to decline an additional 5% in 1975 due to the conversion of the General Motors Van Nuys plant to water-base paints. Emissions are also assumed to decrease 10% in 1977 due to the closure of a Chrysler plant. A growth factor of 3.5% per year is applied to this source type for the period 1974 to 1978 (BEA 1975).

Architectural surface coating is also a major organic solvent source category. RHC emissions from architectural surface coating are assumed to grow at the same rate as population. SCAQMD Rule 481, passed in October 1977, limits the sale of petroleum-base coatings. We have assumed that this rule caused a 10% decrease in architectural surface coating emissions from 1977 to 1978.

Domestic solvent use was assumed to be uncontrolled from 1974 to 1978 and was grown according to population growth during that period. The report by Trijonis and Arledge (1976) does not contain a reactivity factor for this specific source type; we have assumed a reactivity factor of 0.80.

The drycleaning industry has historically substituted synthetic solvents with zero reactivity for the traditional petroleum-base solvents. Certain types of drycleaning, however, require petroleum-base solvents. For the period 1974 to 1978, we have assumed that the use of petroleum-base solvents in drycleaning has increased according to the index of manufacturing for service industries in Los Angeles, 3.5% annually (BEA 1975).

Degreasing has also been controlled historically by the substitution of zero reactivity 1,1,1-trichloroethane for the reactive solvent trichloroethylene (TCE). Again, however, TCE is required for certain purposes. We have assumed that the small amount of TCE emissions remaining in 1974 has grown according to the service industry index in Los Angeles, 3.5% annually from 1974 to 1978 (BEA 1975).

Organic solvent emissions from printing include emissions from both flexigraphic and rotogravure printing. We have assumed that this category

is uncontrolled for the period 1974 to 1978 and that emissions have grown according to the manufacturing index for printing in Los Angeles, 3.3% annually (BEA 1975).

Miscellaneous organic solvent use includes the electronic industry and manufacturing of soaps, fertilizers, explosives, and pesticides. This category was assumed to grow according to the index of miscellaneous manufacturing in Los Angeles, 3.5% annually from 1974 to 1978 (BEA 1975). Trijonis and Arledge (1976) did not list a specific reactivity for this source type; we have assumed a reactivity of 0.50.

Petroleum Refining/Production

RHC emissions from petroleum refining/production are assumed to be constant from 1965 to 1977 (BEA 1975; Chatfield 1975; Trijonis et al. 1976; Thomas 1980). It is also assumed that petroleum production emissions stayed constant from 1977 to 1978. Refinery emissions, however, were reduced 12.5% from 1977 to 1978 due to the emplacement of secondary seal controls (Thomas 1980).

Petroleum Marketing

The petroleum marketing category includes three source types: marine loading of petroleum products, fugitive emissions from natural gas transmission, and gasoline marketing. Gasoline marketing constitutes by far the largest of these three; it contributes 80% of the RHC emissions in this category.

We have assumed marine loading emissions to be constant over the period 1965 to 1978 (BEA 1975; Thomas 1980). Fugitive emissions from natural gas transmission are assumed to increase from 1965 to 1978 according to growth in natural gas usage (Wood 1980).

Significant controls have affected gasoline marketing emissions in Los Angeles. All service stations were assumed to already have 35% control for underground tanks by 1965 due to submerged fill regulations (Thomas 1980). We have assumed that there was an additional 95% control of underground tanks in 1976 due to the introduction of balanced

submerged fill. Balanced automobile tank filling controls do not affect our emission estimates because these controls do not start until 1979. In addition to the impact of controls, gasoline marketing emissions are affected by growth in gasoline sales. We have obtained this growth data from CBE (1980). These data basically show that gasoline sales increased 40% from 1965 to 1973, decreased 5% in 1974, and increased 19% from 1974 to 1978.

Other RHC Sources

This category is a small but growing part of stationary RHC emissions. It represented 4.9% of stationary RHC emissions in 1965 and 8.2% in 1978. The category consists of numerous small types of hydrocarbon sources discussed below.

One source type is non-solvent RHC emissions from chemical, metallurgical, mineral, and miscellaneous industries. These emissions are assumed to be uncontrolled and are grown according to the manufacturing index for Los Angeles (BEA 1975).

Sanitary landfills are a very large source of total hydrocarbons (approximately 800 tons/day), but nearly all the emissions are methane. We have assumed a reactivity factor of 0.001 for these emissions based on data compiled by Taback et al. (1978) and Trijonis and Arledge (1976). We have also assumed sanitary landfill emissions to be constant from 1965 to 1978.

Domestic and industrial fuel combustion is a very small source type with low reactivity. This category is uncontrolled and emissions are grown by the manufacturing index for Los Angeles (BEA 1975).

Waste burning is also a very minor source with low reactivity. We have assumed this category to be uncontrolled from 1965 to 1978 although very recent legislation will limit waste burning. This category is grown by population from 1965 to 1978.

We have assumed that several other very small source types are constant from 1965 to 1978. These source types include structural fires, food processing, agricultural activity, and pesticides.

STATIONARY NO_X SOURCES

Stationary source NO_x emissions arise from two categories: electric power plants and other stationary sources (basically residential/commercial/industrial fuel combustion). Table A-2 lists our emission trend estimates for these two categories. In deriving these emission trends we have used the comprehensive stationary source inventory for NO_x compiled by Bartz et al. (1974) as a base year inventory. The emissions for that inventory are projected backward and forward in time as discussed below.

Electric Power Plants

Year-to-year estimates of electric power plant emissions for Los Angeles have been compiled by Grissinger (1980). We have simply used his data to compute trends in power plant NO_x. These trends represent partial NO_x controls installed in the late 1960s and early 1970s, yearly load variations from 1965 to 1978, and yearly shifts in fuel types from 1965 to 1978.

Other Stationary NO_X Sources

Nearly all of this (uncontrolled) category consists of NO_x emissions from residential/commerical/industrial fuel combustion. In compiling trends for fuel usage, it is convenient to separate out refineries from the remainder of industrial activity. NO_x emissions from refinery fuel combustion are assumed to be constant from 1964 to 1978 (BEA 1975; Chatfield 1975; Trijonis et al. 1976). Natural gas combustion emissions from residential, commercial, and non-refinery industrial activities are calculated from sales figures of the Southern California Gas Company from 1968 to 1978 (Wood 1980). Natural gas emissions from these activities prior to 1968 are grown by population. In addition to natural gas usage there is some fuel oil usage in the commercial and industrial sectors. Trends in the small contribution from fuel oil combustion are calculated using data in DOC (1974-1977) and Bartz et al. (1974).

NO_x emissions from miscellaneous industrial processes constitute a very small (uncontrolled) source category. This category is grown according to the manufacturing index for Los Angeles from 1965 to 1978 (BEA 1975).

TABLE A-2. SUMMARY OF EMISSION TRENDS FROM STATIONARY SOURCES OF NO_x.

YEAR	NO_x EMISSIONS BY SOURCE CATEGORY (TONS/DAY)		
	Power Plants	Other Stationary Sources	Total
1965	197	211	408
1966	213	216	429
1967	219	216	435
1968	228	216	444
1969	234	216	450
1970	153	242	395
1971	147	242	389
1972	141	242	383
1973	170	246	416
1974	123	263	386
1975	135	274	409
1976	114	274	388
1977	170	278	448
1978	140	285	425

MOBILE SOURCES OF HYDROCARBONS AND NO_x

Tables A-3 and A-4 list our emission trend estimates for nine types of mobile sources. Table A-3 is for RHC; Table A-4 is for NO_x. Our discussion of methods for calculating emission trends is organized below according to the six traffic sources (passenger cars, light-duty trucks, medium-duty trucks, gasoline heavy-duty trucks, diesel heavy-duty trucks, and motorcycles) and three non-traffic sources (aircraft, ships/trains, and off-road/utility equipment).

Traffic Sources

Our emission calculations for each of the six types of motor vehicle traffic sources are based on output from the MOBILE2 computer program,

TABLE A-3. SUMMARY OF RHC EMISSION TRENDS FROM MOBILE SOURCES (TONS/DAY).

Year	Passenger Cars	Light-Duty Trucks	Medium-Duty Trucks	Gasoline Heavy-Duty Trucks	Diesel Heavy-Duty Trucks	Motor-cycles	Air-Craft	Ships/ Trains	Off-Road and Utility Vehicles	Totals
1965	879	133	13	40	6	7	22	11	55	1166
1966	875	132	13	40	7	7	23	11	57	1165
1967	852	128	14	41	7	7	24	11	60	1144
1968	830	125	14	42	7	8	26	11	61	1124
1969	813	123	14	43	8	8	27	11	64	1111
1970	790	120	13	41	8	8	28	11	66	1085
1971	759	116	13	41	8	9	29	11	69	1055
1972	734	112	13	41	8	9	28	11	72	1028
1973	709	107	13	41	9	10	28	11	74	1002
1974	635	98	11	37	9	9	27	11	73	910
1975	608	94	11	36	9	10	27	11	74	880
1976	565	88	10	34	9	10	27	11	76	830
1977	529	81	9	33	10	10	27	11	78	788
1978	492	76	8	30	10	11	27	11	81	746

TABLE A-4. SUMMARY OF NO_x EMISSION TRENDS FROM MOBILE SOURCES (TONS/DAY).

Year	Passenger Cars	Light-Duty Trucks	Medium-Duty Trucks	Gasoline Heavy-Duty Trucks	Diesel Heavy-Duty Trucks	Motor-cycles	Air-Craft	Ships/ Trains	Off-Road and Utility Vehicles	Totals
1965	383	58	12	34	89	*	11	27	58	672
1966	407	62	13	36	94	*	12	27	59	710
1967	446	68	14	38	98	*	12	27	61	764
1968	483	74	15	40	103	*	13	27	62	817
1969	520	79	15	42	109	*	13	27	63	868
1970	560	86	17	46	114	*	14	27	64	928
1971	605	92	18	51	120	*	14	27	66	993
1972	638	96	20	55	126	*	14	27	67	1043
1973	665	99	21	60	133	*	14	27	68	1087
1974	603	89	17	55	118	*	14	27	67	990
1975	597	87	16	56	122	*	14	27	68	987
1976	598	87	15	58	126	*	14	27	69	994
1977	597	87	15	60	131	*	14	27	71	1002
1978	580	87	14	59	131	*	14	27	72	984

*negligible

kindly provided to us by the EPA Ann Arbor Laboratory (Platte 1980). The latest California-specific version of MOBILE2 contains very substantial improvements over previous MOBILE1 programs for California (EPA 1978; ARB 1980); these improvements are particularly significant when estimating historical emission trends (rather than future emission trends). The MOBILE2 program was run with the California age/mileage distribution as well as with hot/cold start mixes and temperature/humidity corrections specific to Los Angeles. The hot/cold start mix is 17% cold start VMT and 26% hot start VMT for non-catalyst cars; the mix is 26% cold start VMT and 17% hot start VMT for catalyst cars (LARTS 1979). The temperature and relative humidity are 75^{0} Farenheit and 60%, respectively (NOAA 1977).

The output of the MOBILE2 program is a set of fleet-averaged emission factors for each of the six vehicle types, for each year, and for various specific speeds. To obtain a total fleet-averaged emission factor for each year and for each vehicle type, the factors for the individual speeds are weighted by the speed distributions listed in the right hand side of Table A-5 (LARTS 1971, 1979). Total emissions for each vehicle type each year are calculated using the total VMT trends listed in the left hand side of Table A-5 (Trijonis et al. 1976; LARTS 1979; SCAG 1979) and the VMT distribution by vehicle type listed as follows (LARTS 1980):

Passenger cars -- 80.4%
Light-duty trucks -- 12.1%
Medium-duty trucks -- 1.4%
Gasoline heavy-duty trucks -- 2.6%
Diesel heavy-duty trucks -- 2.6%
Motorcycles -- 0.9%

Non-Traffic Mobile Sources

There are three major groups of non-traffic mobile sources: aircraft, ships/trains, and off-road/utility equipment. For all three groups, base year emissions are taken from Trijonis and Arledge (1976) for hydrocarbons and Trijonis et al. (1975) for NO_x. Growth and control factors are applied to these base year emissions as described below.

TABLE A-5. LONG-TERM TRENDS IN TRAFFIC (VMT) PARAMETERS.

YEAR	TOTAL VMT (billion miles per year)	PERCENT OF VMT BY SPEED CATEGORY 26 mph	45 mph	55 mph	65 mph
1965	41.6	58.1	14.2	----	27.7
1966	43.5	57.1	14.6	----	28.3
1967	45.6	56.1	14.9	----	29.0
1968	47.8	55.1	15.2	----	29.7
1969	50.0	54.1	15.6	----	30.3
1970	52.4	53.1	15.9	----	31.0
1971	45.9	52.0	16.3	----	31.7
1972	57.5	51.0	16.7	----	32.3
1973	60.3	50.0	17.0	----	33.0
1974	57.6	50.0	17.0	33.0	----
1975	59.7	50.0	17.0	33.0	----
1976	61.8	50.0	17.0	33.0	----
1977	64.0	50.0	17.0	33.0	----
1978	66.1	50.0	17.0	33.0	----

In the case of aircraft, we consider jet and propeller planes separately. Jet traffic is assumed to grow at a 9% annual rate, and propeller traffic is assumed to grow at a 4% annual rate from 1965 to 1972 (Trijonis et al. 1976). Aircraft traffic levels are assumed to be constant from 1972 to 1978 (FAA 1980). Jet aircraft emissions are controlled 30% between 1970 and 1974 due to the combustion chamber redesign for JT8D engines (Trijonis 1972). This control also had the effect of increasing total jet NO_x emissions by 6%.

The emissions from ships and railroads are assumed to be constant from 1965 to 1978 (Trijonis et al. 1976; AAR 1979).

Emissions from off-road vehicles and from commercial/residential utility equipment are uncontrolled over the period 1965 to 1978. Off-road

vehicle use is assumed to grow at the same rate as VMT (see previous Table A-5). The use of utility equipment is assumed to grow at the same rate as population.

REFERENCES FOR APPENDIX A

AAR (American Association of Railroads), "Statistics of Railroads of Class I in the United States," Association of American Railroads, Economics and Finance Department, American Railroads Building, Washington, D.C., 1979.

APCD (Air Pollution Control District), "Profile of Air Pollution Control," Air Pollution Control District, County of Los Angeles, California, 1971.

ARB (Air Resources Board), "Procedure and Basis for Estimating On-Road Motor Vehicle Emissions," Califronia Air Resources Board, Technical Services Division, Sacramento, California, January 1980.

Bartz, D.R. et al., "Control of Oxides of Nitrogen from Stationary Sources in the South Coast Air Basin," Prepared at KVB, Tustin, California (KVB 5800-179), For Air Resources Board, State of California (ARB 2-1471), Sept. 1974.

BEA (Bureau of Economic Ananysis), "Population and Economic Activity in the U.S. and SMSA's; Historical and Projected 1950-2020," U.S. Department of Commerce, Washington, D.C., 1975.

CBE (California Board of Equalization), Sacramento, California, Personal Communication, 1980.

Chatfield, H., Los Angeles County Air Pollution Control District, Personal Communication, October 1975.

Dimitriades, B., "The Concept of Reactivity and Its Possible Applications in Control," Proceedings of the Solvent Reactivity Conference, EPA-650/3-74-010, November 1974.

DOC (Department of Commerce), "Annual Survey of Manufactures", Washington, D.C., 1974-1977.

EPA (Environmental Protection Agency), "Mobile Source Emission Factors," National Technical Information Service, PB-295 672, Springfield, Virginia, March 1978.

FAA (Federal Aviation Administration), Washington, D.C., Personal Communication from Howard Maddox, Air Traffic Div., L.A. Int. Airport, 1980.

Grissinger, J., California Air Resources Board, El Monte, California, Personal Communication of Data, 1980.

LARTS (Los Angeles Regional Transportation Study), "LARTS Base Year Report, 1967 Origin-Destination Survey," Los Angeles, California, December 1971.

LARTS (Los Angeles Regional Transportation Study), "The 1976 Urban and Rural Travel Surven, Volume IV, Summary of Findings: Travel Data," Los Angeles, California, October 1979.

LARTS (Los Angeles Regional Transportation Study), Los Angeles, California, Personal Communication of Data from Charles Bare, 1980.

NOAA (National Oceanic and Atmospheric Administration),"Climatic Atlas of the United States," U.S. Department of Commerce, Washington, D.C., 1977.

Platte, L., U.S. EPA, Office of Mobile Source Air Pollution Control, Ann Arbor, Michigan, Personal Communication, 1980.

SCAG (Southern California Association of Governments), "First Annual Reasonable Further Progress Report on the South Coast Air Quality Management Plan," Southern California Association of Governments and South Coast Air Quality Management District, Los Angeles, California, July 1, 1980.

Taback H. et al., "Control of Hydrocarbon Emissions from Stationary Sources in the California South Coast Air Basin," Prepared at KVB (KVB 5804-714), Tustin, California, for California Air Resources Board (ARB 5-1323), Sacramento, California, June 1978.

Thomas, G., South Coast Air Quality Management District, Calfornia, Personal Communication, 1980.

Trijonis, J., "An Economic Air Pollution Control Model -- Application: Photochemical Smog in Los Angeles County in 1975," Ph.D. Thesis, California Institute of Technology, Pasadena, Calfornia, 1972.

Trijonis, J. and K. Arledge, "Utility of Reactivity Criteria in Organic Emission Control Strategies, Application to the Los Angeles Atmosphere," EPA-600/3-76-091, U.S. EPA, Research Triangle Park, NC, August 1976.

Trijonis, J. et al., "An Implementation Plan for Suspended Particulate Matter in the Los Angeles Region," Prepared at TRW Inc., Contract No. 68-02-1384, to the U.S. EPA, March 1975.

Trijonis, J. et al., "Emissions and Air Quality Trends in the South Coast Air Basin," EQL Memo No. 16, Environmental Quality Laboratory, California Institute of Technology, Pasadena, California, January 1976.

Weiss, S., South Coast Air Quality Management Discrict, California, Personal Communication, 1980.

Wood, W., California Energy Commission, Sacramento, California, Personal Communication of Data, 1980.

APPENDIX B

ANALYSIS OF A REPORTED ANOMALY IN OZONE TREND DATA FOR LOS ANGELES COUNTY

Kinosian (1980) and Duckworth et al. (1980) have reported an apparent "glitch" in ozone trend data for Los Angeles County during the early 1970s. Specifically, in examining ozone trend data at Azusa, Pomona, and Pasadena, they found a "precipitous decrease of the measured ozone concentrations from 1970 to 1972 [that] cannot be explained by either meteorological factors or by change of emissions of ozone precursor pollutants". Supposedly, this glitch might have been produced by an undocumented change in monitoring practices within Los Angeles County. We must investigate the possibility of this glitch carefully, because it could have major implications for our EKMA validation studies at Los Angeles County locations (Azusa and DOLA).

In examining historical trends for a possible discontinuity, it is useful to consider data with better temporal resolution than yearly average data. Using yearly averages, it takes three years of data for the entire glitch to manifest itself. For example, if a monitoring discontinuity occurred in 1971, the entire effect would be apparent in data for the years 1970 and 1972, the first complete years of data before and after the discontinuity. Over the course of three years, however, significant ozone changes can also be caused by historical emission trends; these emission caused changes could be confused with the effects of a monitoring discontinuity.

To obtain better temporal resolution in the ozone trend data we have decided to use 1-year moving averages of quarterly means of daily maximal ozone concentrations. With this type of trend index, a monitoring discontinuity would be revealed as a sharp decline occurring over one year (four quarters). Figures B1 and B2 present trends for this index at ten locations that have nearly continuous ozone data for the period 1964 to 1975. Figure B1 is for five coastal/central sites; Figure B2 is for five valley/inland sites. Each figure contains four Los Angeles County locations and one Orange County location (Anaheim in Figure B1 and La Habra in Figure B2).

Scrutiny of Figures B1 and B2, as well as consideration of other information, leads us to doubt that there really is a monitoring discontinuity

Figure B1. Four-quarter moving averages of daily maximal one-hour ozone concentrations at five coastal/central locations.

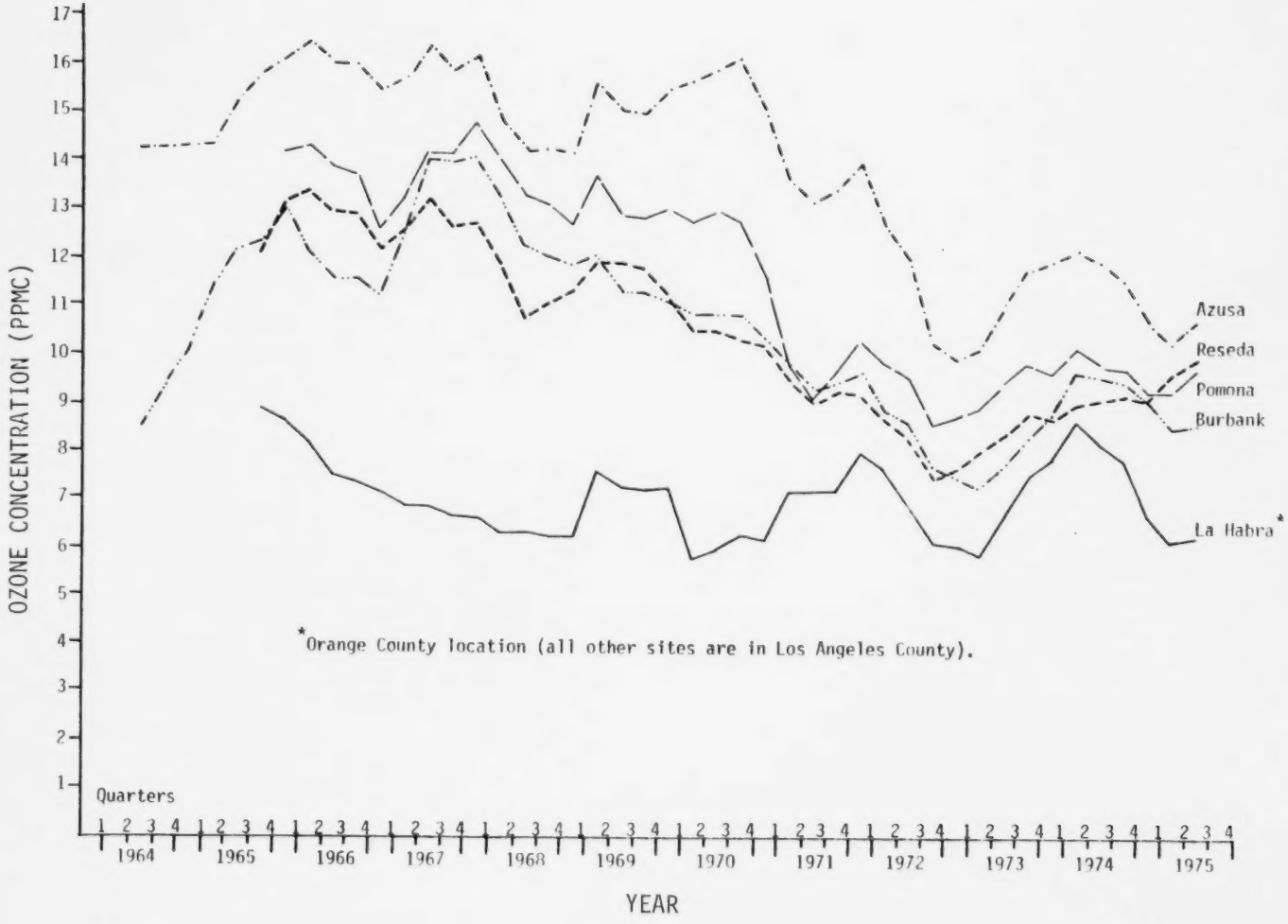

Figure B2. Four-quarter moving averages of daily maximal one-hour ozone concentrations at five valley/inland locations.

in the Los Angeles County ozone data. Our doubt is based on the following observations:

- The hypothesis of a monitoring discontinuity in Los Angeles would make most sense if all Los Angeles County sites showed a glitch which was not apparent in the Orange County data. However, examining Figures B1 and B2, one finds that only two Los Angeles County sites -- Azusa and Pomona -- show an abnormal decline in ozone during the period 1970 to 1972. The other six monitoring sites in Los Angeles County exhibit declining ozone trends during 1970-1972, but these declines do not appear abnormal because they represent a smooth continuation of historical ozone decreases prior to 1970. Furthermore, Anaheim (in Orange County) shows a declining ozone trend over the decade and during 1970-1972 similar to that at the other six Los Angeles County stations.* Thus, there is not a uniform abnormality among all Los Angeles County sites; in fact, trends at six Los Angeles County sites closely parallel trends at Anaheim and do not show signs of a glitch.

- The hypothesis of a monitoring discontinuity would make most sense if the drop in our ozone index occurred over one year (four quarters). To the contrary, the sharp decline in ozone at Azusa and Pomona occurs over a two year period (4th quarter of 1970 to the 4th quarter of 1972).

- Ozone trend data at two non-Los Angeles County sites in the eastern basin (Riverside and San Bernardino) seem to confirm the 1970-1972 ozone drop at Azusa and Pomona as being real rather than a glitch. Data at these two non-Los Angeles County sites do not provide a continuous record because of a monitor relocation at Riverside during the 3rd quarter of 1972 and questions regarding the quality of the 1972 San Bernardino data (Trijonis 1980; Zeldin 1978). Nevertheless, the available ozone data at Riverside and San Bernardino do exhibit a significant drop from 1970 to the middle of 1972 (although the drop is not quite as great as the decline observed at Azusa and Pomona).

- The glitch observed by Duckworth et al. and Kinosian may be due to the particular sites they analyzed and emphasized by their method of data analysis. The sites they examined were Azusa, Pomona, and Pasadena. As noted previously, Azusa and Pomona are the only two sites at which we see an abnormal ozone drop. Pasadena is not a valid trend site because of two significant monitor relocations (in 1968 and 1972). Also, the analysis methods employed by Duckworth et al. and Kinosian might serve to emphasize the glitch. Each investigator considered an

*We must admit that La Habra (in Orange County) does not show an ozone decrease during 1970-1972. However, La Habra may be a special case because it is the inland ozone site affected by the most rapidly growing part of the basin.

"adjustment" or "surrogate" index for ozone based on a regression equation. Duckworth et al. regressed ozone to meteorology (temperature aloft); Kinosian regressed ozone to ambient NO_2 concentrations. The regressions by Duckworth et al. were based on the years 1973-1979; the regressions by Kinosian were based on the years 1971-1979. Each investigator noted a glitch in the sense that the data for 1964-1971 (in the case of Duckworth et al.) and for 1964-1970 (in the case of Kinosian) did not fit their regression relationship. However, one should not be surprised that data for the earlier years depart from a regression relationship based only on data for the later years. One particularly should not be surprised if the data depart from the regression equation when we are considering Azusa and Pomona during the early 1970s. It has often been suggested that Azusa and Pomona went over the peak of the "ozone isopleth hill" in 1970, and therefore started to show ozone improvements after 1970 (Kinosian and Paskind 1973; Paskind and Kinosian 1974; Dickenson and Davidson 1976; Davidson 1979; Trijonis 1980). Thus, the "glitch" observed by Duckworth et al. and Kinosian may be due to their choice of sites, emphasized by their data analysis methods, and related to the historical placement of Azusa and Pomona on the "ozone isopleth hill".

In summary, we cannot be sure that there is no glitch in the Los Angeles County ozone data due to a discontinuity in monitoring procedures. Based on the above discussion, however, we doubt that there is a glitch. There certainly is no consistent discontinuity occurring at all Los Angeles County sites. There may be a problem at Azusa and Pomona, but we find it hard to imagine why the error would occur only at those two sites and why it would take two full years to manifest itself. It seems more reasonable to conclude that those two sites both measured an unusual (but real) ozone drop in eastern Los Angeles County from 1970 to 1972.

REFERENCES FOR APPENDIX B

Davidson, A., "Ozone Trends in the South Coast Air Basin of California," Presented at the APCA Specialty Conference on: Ozone/Oxidants, Interactions with the Total Enviornment, Houston, Texas, October 1979.

Dickenson, J. and A. Davidson, "Air Quality Trends in the Southern California Air Pollution Control District," Presented before the Southern California Air Pollution Control District Board at Pomona, California, January 9, 1976.

Duckworth, S. et al., "Analysis of Meteorological and Other Factors Influencing Air Quality Trends," Presented at the Conference on Air Quality Trends in the South Coast Air Basin, Pasadena, California, Feb. 21, 1980.

Kinosian, J., "Confirmation of Ozone Trends," Presented at the Conference on Air Quality Trends in the South Coast Air Basin, Pasadena, California, February 21-22, 1980.

Kinosian, J. and J. Paskind, "Hydrocarbon, Oxides of Nitrogen and Oxidant Trends in the South Coast Air Basin, 1963-1972," California Air Resources Board, Technical Services Division, Sacramento, California, 1973.

Paskind J. and J. Kinosian, "Hydrocarbon, Oxides of Nitrogen and Oxidant Pollution Relationships in the Atmosphere Over California Cities," Presented at the 67th Annual Meeting of the Air Pollution Control Association, Denver, Colorado, June 9-13, 1974.

Trijonis, J., "Oxidant and Precursor Trends in the Metropolitan Los Angeles Region: An Update," Presented at the Conference on Air Quality Trends in the South Coast Air Basin, Pasadena, California, February 21-22, 1980.

Zeldin, M., Meteorological Consultant, San Bernardino, California, Personal Communication, 1978.

APPENDIX C

PROPANE AND ETHANE FRACTIONS IN AMBIENT NMHC CONCENTRATIONS FOR LOS ANGELES

As noted in Chapters 4 and 5 of this report, it is desirable to adjust ambient 6-9 AM NMHC/NO_x ratios to be as equivalent as possible to EKMA NMHC/NO_x ratios. One of the adjustments concerns the relative reactivity of ambient NMHC and EKMA NMHC. As a first approximation in accounting for reactivity differences, we should adjust for the fact that ambient NMHC contains significant amounts of the nearly nonreactive compounds, ethane and propane, while the smog chamber studies on which EKMA is based contain very little (approximately 1%) ethane and propane.

To make the adjustment for ethane and propane fractions, we need to know the approximate percentage (as ppmC) of ethane and propane in ambient NMHC concentrations for Los Angeles. Table C-1 summarizes the percent of ethane and propane in ambient 6-9 AM NMHC samples taken at various Los Angeles sites during various years. In compiling Table C-1, we have considered all possible data sources that could be found in the literature. To some extent, the plethora of data in Table C-1 is an overkill. We thought, however, that it would be a useful exercise to identify all available historical data sources regarding NMHC composition in Los Angeles. These data sources might fruitfully serve as the basis for a future study of historical trends in ambient NMHC composition within Los Angeles.

It should be noted that, in compiling Table C-1, problems were encountered regarding the completeness of the ambient NMHC composition data. Those problems and the assumptions we used to counteract them are described below:

- A major problem in data compilation is the incompleteness of hydrocarbon composition data reported in the literature. In some cases, composition data are given only for C_2-C_5 hydrocarbons; in other cases, composition data are given for C_2-C_{11} or for C_2-C_{18} hydrocarbons. When data are missing for a particular compound, it can mean either that the compound was not detected in the chemical analysis or that the compound was not analyzed for. Judgement had to be used to decide which of the two possibilities was most appropriate for the "missing" compounds.

TABLE C-1. PERCENT OF ETHANE AND PROPANE IN AMBIENT LOS ANGELES NMHC CONCENTRATIONS.

SITE	TIME PERIOD	DATA SOURCE	PERCENT ETHANE AND PROPANE AS PPMC		
			% Ethane	% Propane	% Propane & Ethane
Downtown Los Angeles	1967: Sep-Nov (5am-6am, 7am-9am)	Altshuller, et al. (1971)	5.7	3.3	9.0
	1968: Sep-Nov (7am-8am)	Kopczynski, et al. (1972)	4.8	3.5	8.3
	1970: Fall (6am-8am)	Bonzmassa and Mayrsohn (1972)	4.8	4.6	9.4
	1971: Aug-Oct (8am-10am)	Bonamassa and Mayrsohn (1972)	4.8	4.3	9.1
	1971-1972: Dec '71-Jan '72 8am-9am)	SCAQMD (1974)	3.2	3.6	6.8
	1973: Mar-Aug (8am-9am)	SCAQMD (1974)	2.2	2.7	4.9
	Nov 5 (8:23 am)	Calvert (1976)	3.2	3.6	6.8
	1974: Jun 25-Jul 18 (6am-9am)	Mayrsonn et al (1975)	3.4	3.2	6.6
	1976: Jun 21-Sep 2 (6am-9am)	Mayrsohn et al. (1977)	4.1	4.3	8.4
	1977: Jun 21-Aug 16 (6am-9am)	ARB (1977)	5.0	5.5	10.5
Azusa	1967: Sep-Nov (5am-6am, 7am-9am)	Altshuller (1971)	5.6	3.8	9.4
	1970: Fall (6am-8am)	Bonamassa and Mayrsohn (1972)	5.8	5.1	10.9
	1971: Aug-Oct (8am-10am)	Bonamassa and Mayrsohn (1972)	5.8	4.8	10.6
	1974: Jun 18-Sep 5 (6am-9am)	Mayrsohn et al. (1975)	3.3	2.8	6.1
	1975: Aug 4-Sep 3 (6am-9am)	Mayrsohn et al. (1976)	3.7	3.0	6.7
	1976: Jun 14-Aug 26 (6am-9am)	Mayrsohn et al. (1977)	3.9	4.0	7.9
	1977: Jun 21-Aug 16 (6am-9am)	ARB (1977)	4.2	4.8	9.0
Long Beach	1974: Jun 24-Sep 15 (6am-9am)	Mayrsohn et al. (1975)	4.5	5.8	10.3
	1975: Jun 10-Jul 24 (6am-9am)	Mayrsohn et al. (1976)	6.1	7.8	13.9
	1976: Jun 14-Sep 1 (6am-9am)	Mayrsohn et al. (1977)	6.4	8.4	14.8
El Monte	1974: Jul 1-Sep 5 (6am-9am)	Mayrsohn et al. (1975)	3.7	5.3	9.0
	1975: Jul 29-Sep 25 (6am-9am)	Mayrsohn et al. (1976)	4.8	4.2	9.0
Upland	1974: Jun 24-Sep 5 (6am-9am)	Mayrsohn et al. (1975)	2.8	2.2	5.0
	1975: Jun 16-Aug 1 (6am-9am)	Mayrsohn et al. (1976)	3.4	3.2	6.6
	1976: Jun 15-Sep 2 (6am-9am)	Mayrsohn et al. (1977)	4.6	4.0	8.6
Riverside	1968: Sep 24 (7:30 am)	Stephens et al. (1969)	2.3	1.0	3.3

- Concentration data are not available for hydrocarbons with more than eighteen carbon atoms per molecule. Thus, we were forced to assume that the total NMHC concentration equals the C_2-C_{18} hydrocarbon concentration. Equating the C_2-C_{18} hydrocarbon compounds to the total NMHC concentration should not introduce a significant error since the greater-than-C_{18} hydrocarbons should form only a small proportion of the atmospheric NMHC composition.

- When only partial composition data were available, the available hydrocarbons were assumed to form the same percent of the total NMHC composition (in ppmC) as in those years for which complete C_2-C_{18} data were available. For example, if only C_2-C_5 concentrations are known for Los Angeles in 1973, and if C_2-C_5 form 41% of the total NMHC concentration for Los Angeles in 1976 (the year for which complete C_2-C_{18} data are available), then C_2-C_5 is assumed for form 41% of the total NMHC concentration in 1973.

For the purposes of this study, the most relevant finding in Table C-1 is that ethane and propane constitute approximately 10% of ambient NMHC. Thus, in Chapter 4, we adjust the ambient NMHC/NO_x ratio downward by 10% to account for the extra ethane and propane in ambient NMHC as compared to EKMA-equivalent NMHC.

REFERENCES FOR APPENDIX C

Altshuller, A.P. et al., "Hydrocarbon Composition of the Atmosphere of the Los Angeles Basin--1967," Envir. Sci. Technol., Vol. 5, No. 10, October 1971.

ARB (Air Resources Board), Source Reconciliation of Atmospheric Hydrocarbons in the South Coast Air Basin, June-August 1977, State of California, Air Resources Board, Sacramento, California, 1977.

Bonamassa, F., and H. Mayrsohn, Studies of Hydrocarbons in Transit in the Los Angeles Basin: Aug-Oct 1971, Unpublished Report, State of California, Air Resources Board, Sacramento, California, February 1972.

Calvert, J., "Hydrocarbon Involvement in Photochemical Smog Formation in Los Angeles Atmosphere," Envir. Sci. Technol., Vol. 10, No. 3, March 1976.

Kopczynski, S. et al., "Photochemistry of Atmospheric Samples in Los Angeles," Envir. Sci. Technol., Vol. 6, No. 4, April 1972.

Mayrsohn, H. et al., Atmospheric Hydrocarbon Concentrations: June - September 1974, State of California, Air Resources Board, Sacramento, California, April 1975.

Mayrsohn, H. et al., Atmospheric Hydrocarbon Concentrations: June-September 1975, State of California, Air Resources Board, Sacramento, California, January 1976.

Mayrsohn, H. et al., Atmospheric Hydrocarbon Concentrations: June-September 1976, State of California, Air Resources Board, Sacramento, California, January 1977.

SCAQMD (Southern California Air Quality Management District), Air Quality & Meteorology, 1974 Annual Report, Air Pollution Control District, County of Los Angeles, 1974.

Stephens, E. et al., "Distribution of Light Hydrocarbons in Ambient Air," J. APCA, Vol. 19, No. 12, December 1969.